PB 185563

TRACOR Document
Number 69-579-U
Project Serial
Number 004-009
Task Number 10

APPLICABILITY OF METAL OXIDES TO THE DEVELOPMENT OF NEW PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

FINAL REPORT

VOLUME II

Section 8

Contract PH 86-68-68

Submitted to:

Process Control Engineering Program
National Air Pollution Control
Administration
5710 Wooster Pike
Cincinnati, Ohio 45227

31 July 1969

TRACOR

6500 Tracor Lane, Austin, Texas 78721, AC 512 926-2800

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

1039

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

TRACOR Document
Number 69-579-U
Project Serial
Number 004-009
Task Number 10

APPLICABILITY OF METAL OXIDES TO THE DEVELOPMENT OF NEW PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

FINAL REPORT

VOLUME II

Section 8

Contract PH 86-68-68

Submitted to:

Process Control Engineering Program
National Air Pollution Control
  Administration
5710 Wooster Pike
Cincinnati, Ohio   45227

31 July 1969

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

8.1 UNABRIDGED TECHNICAL MEMORANDUMS

8.1.1 Technical Memorandums on Thermodynamic Studies

No table of contents in original copy.

Copy made for Chemistry Files

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

1 May 1968

K. Schwitzgebel
P. Lowell

TECHNICAL MEMORANDUM 004-009-Ch1

ESTIMATION METHODS FOR HEAT OF FORMATION AT 25° C

A. SURVEY

The attempts to correlate or to predict heats of formation of inorganic compounds can be divided into two groups.

The authors of the first group try to find linear relations between the heat of formation of chemically similar compounds. Such attempts have been proposed by Karapetjanc (1), Hoppe (2), Fomin (3), and Westland (4).

The authors of the second group all base their methods on the work of L. Pauling (6). Pauling describes the heat of formation as additional ionic bond energy and assigns to each element a specific electronegativity. Each element is characterized by one parameter. Anderson and Bromley (7) refined Pauling's equation by adding to each element a second characteristic factor. In this way they could calculate the heat of formation for a set of halides. The average deviation obtained for 22 metal halides was 0.93 kcal/mole, with errors for certain fluorides up to 10 kcal/mole. By adding a third characteristic factor Wilcox and Bromley have been able to extend the method to more sophisticated compounds (8).

E. Erdös (5) developed the following method. For the first approximation he set the heat of formation of a salt of the type Me_mYO_{n+1} equal to the sum of the heats of formation of the oxides.

In the second approximation he calculated the heat of reaction of the constituent oxides with the relation

$$-H_r^\circ = (A - X)^{5/3}$$

A and X are parameters which characterize the electronegativity of the cation (A) and the anion (X). The factor 5/3 was found by least square calculation. It differs from the factor 2 used by Pauling and Bromley and coworkers. It is the same for carbonates, sulfates and sulfites.

Our own calculations indicate that the exponent varies with respect to the anion.

It should be pointed out that all these methods are more or less empirical. The method of Wilcox and Bromley is the most general one. E. Erdös' method allows calculation of the heats of formation of the sulfites with greater accuracy.

B. THE METHOD OF L. PAULING (6)

L. Pauling gives in his book, "The Nature of the Chemical Bond," the following equation for the estimation of the heat of formation:

$$-\Delta H_f^\circ = 23 \sum_{\substack{\text{over} \\ \text{all bonds}}} (X_A - X_B)^2 - 55.4\, n_N - 26.0\, n_O \qquad (1)$$

X_A, X_B = electronegativities of the molecules A and B forming a single bond

n_N, n_O = number of nitrogen and oxygen atoms in the compound

The equation is based on the following prerequisites:

1. The equation does not apply to substances containing double or triple bonds.

2. The additional ionic resonance energy from unlike atoms forming covalent bonds is responsible for the heat of formation.

3. The postulate that the geometric mean for the energy of a normal covalent bond between the atoms A and B can be replaced by the arithmetic mean.

4. The energy of the van der Waals stabilization of a substance in its standard state is approximately equal to the van der Waals stablization of the elements from which the substance is formed. Due to these prerequisites, Pauling's equation gives only fairly good results for simple inorganic compounds without double or triple bonds.

C. THE METHOD OF ANDERSON AND BROMLEY

Anderson and Bromley extend Pauling's equation empirically. They use the relation:

$$-\Delta H^\circ_f = n_{AB} (X_A - X_B)^2 + n_A Y_A + n_B Y_B \qquad (2)$$

X and Y are empirically determined parameters for each element and each valence state.

n_{AB} = apparent number of single bonds

n_A = number of atoms of the element A

n_B = number of atoms of the element B

The method is applicable to halides only. It requires that experimental heats of formation of at least two halide compounds be known.

D. THE METHOD OF WILCOX AND BROMLEY

Wilcox and Bromley add an additional factor, found by trial and error, to equation (2):

$$-\Delta H^{\circ}_{f} = n_{AB}\,(X_A - X_B)^2 + n_A\,Y_A + n_B\,Y_B + n_{AB}\,(\frac{W_A}{W_B}) \qquad (3)$$

Each atom or atomic group is characterized by three constants, X_A, Y_A, and W_A. These quantities are determined by the least squares method from experimental data. In order to apply this relation, at least three compounds of an element or an atomic group must be known. Table I summarises the results.

There is more background material available concerning a complete literature search of the compounds under investigation (9), and a detailed paper which describes the mathematics and the computer program used (10). Both papers are ordered, but have not yet been received.

E. THE METHOD OF ERDÖS

Erdos describes the heat of formation of a salt of the type Me_mYO_{n+1} with the following equation:

$$\Delta H^{\circ}_{f} = \Delta H^{\circ}_{f,Me_mO} + \Delta H^{\circ}_{f,YO_n} - (X - A)^c \qquad (4)$$

This means that the heat of formation of the compound Me_mYO_{n+1} was the sum of the heats of formation of the metal oxide Me_mO, the oxyanion YO_n and the heat of reaction $\left[- (X-A)^c\right]$. X and A are parameters which describe the basicity (electropositivity) and the acidity (electronegativity) of the cation and the anion. The exponent c was determined by a least squares error calculation to be 5/3. This value was taken by Erdös to describe the heat of reaction for carbonates, sulfates, and sulfites. Table II gives the calculated and literature values for carbonates, sulfates and the predicted values for the sulfites.

TABLE I

Wilcox and Bromley Tables VI, VII, and VIII

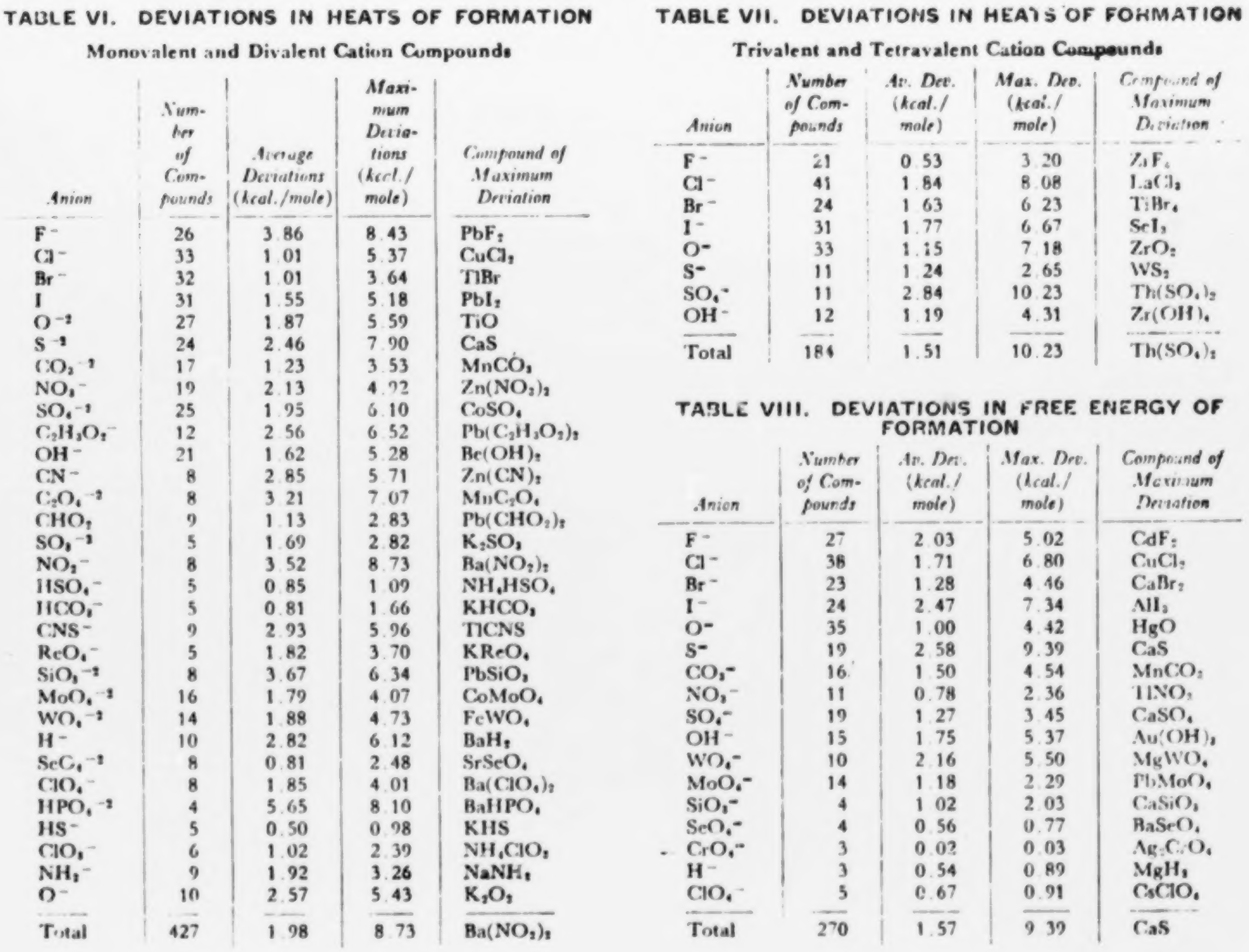


TABLE VI. DEVIATIONS IN HEATS OF FORMATION

Monovalent and Divalent Cation Compounds

Anion	Number of Compounds	Average Deviations (kcal./mole)	Maximum Deviations (kcal./mole)	Compound of Maximum Deviation
F^-	26	3.86	8.43	PbF_2
Cl^-	33	1.01	5.37	$CuCl_2$
Br^-	32	1.01	3.64	TlBr
I	31	1.55	5.18	PbI_2
O^{-2}	27	1.87	5.59	TiO
S^{-2}	24	2.46	7.90	CaS
CO_3^{-2}	17	1.23	3.53	$MnCO_3$
NO_3^-	19	2.13	4.92	$Zn(NO_3)_2$
SO_4^{-2}	25	1.95	6.10	$CoSO_4$
$C_2H_3O_2^-$	12	2.56	6.52	$Pb(C_2H_3O_2)_2$
OH^-	21	1.62	5.28	$Be(OH)_2$
CN^-	8	2.85	5.71	$Zn(CN)_2$
$C_2O_4^{-2}$	8	3.21	7.07	MnC_2O_4
CHO_2	9	1.13	2.83	$Pb(CHO_2)_2$
SO_3^{-2}	5	1.69	2.82	K_2SO_3
NO_2^-	8	3.52	8.73	$Ba(NO_2)_2$
HSO_4^-	5	0.85	1.09	NH_4HSO_4
HCO_3^-	5	0.81	1.66	$KHCO_3$
CNS^-	9	2.93	5.96	TlCNS
ReO_4^-	5	1.82	3.70	$KReO_4$
SiO_3^{-2}	8	3.67	6.34	$PbSiO_3$
MoO_4^{-2}	16	1.79	4.07	$CoMoO_4$
WO_4^{-2}	14	1.88	4.73	$FeWO_4$
H^-	10	2.82	6.12	BaH_2
SeO_4^{-2}	8	0.81	2.48	$SrSeO_4$
ClO_4^-	8	1.85	4.01	$Ba(ClO_4)_2$
HPO_4^{-2}	4	5.65	8.10	$BaHPO_4$
HS^-	5	0.50	0.98	KHS
ClO_3^-	6	1.02	2.39	NH_4ClO_3
NH_2^-	9	1.92	3.26	$NaNH_2$
O^-	10	2.57	5.43	K_2O_2
Total	427	1.98	8.73	$Ba(NO_2)_2$

TABLE VII. DEVIATIONS IN HEATS OF FORMATION

Trivalent and Tetravalent Cation Compounds

Anion	Number of Compounds	Av. Dev. (kcal./mole)	Max. Dev. (kcal./mole)	Compound of Maximum Deviation
F^-	21	0.53	3.20	ZrF_4
Cl^-	41	1.84	8.08	$LaCl_3$
Br^-	24	1.63	6.23	$TiBr_4$
I^-	31	1.77	6.67	ScI_3
$O^{=}$	33	1.15	7.18	ZrO_2
$S^{=}$	11	1.24	2.65	WS_2
$SO_4^{=}$	11	2.84	10.23	$Th(SO_4)_2$
OH^-	12	1.19	4.31	$Zr(OH)_4$
Total	184	1.51	10.23	$Th(SO_4)_2$

TABLE VIII. DEVIATIONS IN FREE ENERGY OF FORMATION

Anion	Number of Compounds	Av. Dev. (kcal./mole)	Max. Dev. (kcal./mole)	Compound of Maximum Deviation
F^-	27	2.03	5.02	CdF_2
Cl^-	38	1.71	6.80	$CuCl_2$
Br^-	23	1.28	4.46	$CaBr_2$
I^-	24	2.47	7.34	AlI_3
$O^{=}$	35	1.00	4.42	HgO
$S^{=}$	19	2.58	9.39	CaS
$CO_3^{=}$	16	1.50	4.54	$MnCO_3$
NO_3^-	11	0.78	2.36	$TlNO_3$
$SO_4^{=}$	19	1.27	3.45	$CaSO_4$
OH^-	15	1.75	5.37	$Au(OH)_3$
$WO_4^{=}$	10	2.16	5.50	$MgWO_4$
$MoO_4^{=}$	14	1.18	2.29	$PbMoO_4$
$SiO_3^{=}$	4	1.02	2.03	$CaSiO_3$
$SeO_4^{=}$	4	0.56	0.77	$BaSeO_4$
$CrO_4^{=}$	3	0.02	0.03	Ag_2CrO_4
H^-	3	0.54	0.89	MgH_2
ClO_4^-	5	0.67	0.91	$CsClO_4$
Total	270	1.57	9.39	CaS

D. E. Wilcox, L. A. Bromley, "Heat and Free Energy of Formation for Simple Inorganic Compounds", Ind. and Eng. Chem., pp. 32-9, (July 1963).

TABLE II

Erdős' Tables I, II, IV

Table I

Heats of Formation of Sulphates at 25°C

Salt	$-\Delta H_f^0$, kcal/mol		Deviation Δ kcal/mol
	experimental[9]	calculated	
Li_2SO_4	342·8	344·4	−1·6
Na_2SO_4	330·9	331·9	−1·0
K_2SO_4	342·7	342·0	+0·7
Rb_2SO_4	340·5	339·2	+1·3
Cs_2SO_4	339·4	337·6	+1·8
$CuSO_4$	184·0	181·9	+2·1
Ag_2SO_4	170·5	167·4	+3·1
$MgSO_4$	305·5	308·1	−2·6
$CaSO_4$	339·2	339·7	−0·5
$SrSO_4$	345·3	346·4	−1·1
$BaSO_4$	350·2	350·3	−0·1
$ZnSO_4$	233·9	234·9	−0·1
$CdSO_4$	221·4	221·8	−0·4
$PbSO_4$	219·5	215·6	+3·9
$MnSO_4$	254·2	256·5	−2·3
$FeSO_4$	220·5	220,7	−0·2
$CoSO_4$	207·5	210·6	−3·1
Average deviation			±*1·5*

[illegible]

Table II

Heats of Formation of Carbonates at 25°C

Salt	$-\Delta H_f^0$, kcal/mol		Deviation Δ kcal/mol
	experimental[9]	calculated	
Li_2CO_3	290·5	288·9	+1·6
Na_2CO_3	270·3	269·3	+1·0
K_2CO_3	273·9	274·8	−0·9
Rb_2CO_3	269·6	271·1	−1·5
Cs_2CO_3	267·4	269·2	1·8
$CuCO_3$	142·2	144·3	−2·1
Ag_2CO_3	121·0	124·1	−3·1
$MgCO_3$	266·0	263·3	+2·7
$CaCO_3$	288·5	287·9	+0·6
$SrCO_3$	291·2	290·1	−1·1
$BaCO_3$	291·3	291·2	−0·1
$ZnCO_3$	194·2	194·1	+0·1
$CdCO_3$	178·7	178·2	0·5
$PbCO_3$	167·3	171·2	−3·9
$MnCO_3$	213·9	211·7	2·2
$FeCO_3$	178·7	178·5	+0·2
$CoCO_3$	172·7	169·7	3·0
Average deviation			±*1·5*

Table IV

Predicted Values of the Heats of Formation of Sulphites at 25°C

Salt	$-\Delta H_f^0$, kcal/mol		Deviation Δ kcal/mol
	experimental[9]	predicted	
Ag_2SO_3		110·1	
$Al_2(SO_3)_3$		665·7	
$BaSO_3$	282·6	281·6	1·0
$BeSO_3$		234·4	
$Bi_2(SO_3)_3$		438·1	
$CaSO_3$		276·3	
$CdSO_3$		164·4	
$Ce(SO_3)_2$		443·8	
$CoSO_3$		155·1	
$CuSO_3$		128·8	
Cs_2SO_3		262·0	
$FeSO_3$		164·3	
$HgSO_3$		114·7	
$In_2(SO_3)_3$		525·3	
K_2SO_3	266·9	267·2	−0·3
Li_2SO_3		278·3	
$MgSO_3$	(241·0)	249·8	(−8·8)
$MnSO_3$		198·2	
Na_2SO_3	260·6	(260·6)	
$NiSO_3$		157·2	
$PbSO_3$		157·6	
$RaSO_3$		281·6	
Rb_2SO_3		263·8	
$Sb_2(SO_3)_3$		424·8	
$Sn(SO_3)_2$		299·2	
$SrSO_3$		279·7	
$Th(SO_3)_2$		490·[illegible]	
Tl_2SO_3		159·9	
$U(SO_3)_2$		455·8	
$ZnSO_3$		179·2	
$Zr(SO_3)_2$		478·4	

E. Erdős, Collection Czech. Chem. Commun., vol. 27, p. 1428 (1962).

For the prediction of heats of formation of sulfites, Erdös used the heat of formation of sodium-sulfite to determine the parameter A (of equation 4) for the sulfite ion.

The acidity of the $CO_3^=$ anion was arbitrarily chosen zero.

F. MASLOV'S RELATION (11)

Maslov gave a very usefull relation to correlate thermodynamic values of salts in different hydration states. Table III characterises these relations.

Table III Data of Maslov

Compound	State	$-\Delta H_f^0$ (in kcal/ mole)	$-\Delta Z_f^0$ (in kcal/ mole)	log K_f	S^0 (in kcal/ / mole · deg.)	C_p^0 (in cal/ / mole · deg.)	n; m; t
$CaSO_3 \cdot nH_2O$	Crystalline	$279 + 71n$	$260.3 + 56.89n$	$190.81 + 41.702n$	$24.3 + 9.866n$	$20.7 + 10.99n$	$n \geq 0$
$CaSO_4 \cdot nH_2O$	»	$341.1 + 71n$	$315.41 + 56.89n$	$231.186 + 41.702n$	$26.6 + 9.866n$	$22.5 + 10.99n$	$n \geq 0$
$CaS_2O_3 \cdot nH_2O$	»		$260.36 + 56.89n$	$191.188 + 41.702n$			$n \geq 0$
$Ca(NO_2)_2 \cdot nCa(OH)_2 \cdot nH_2O$	»	$224.2 + 239.4m + 71n$	$178.33 + 56.89n$	$130.704 + 41.702n$	$44.4 + 9.866n$	$35.7 + 10.99n$	$m \geq 0$
$Ca(NO_3)_2 \cdot nH_2O$ [1]	»	$225.4 + 71n$	$178.9 + 56.89n$	$131.152 + 41.702n$	$41.5 - 9.866n$		$n \geq 0$
$CaHPO_4 \cdot nH_2O$	»	$434 + 71n$	$400.8 + 56.89n$	$293.8 + 41.702n$	$20.3 + 9.866n$		$n \geq 0$
$CaHAsO_4 \cdot nH_2O$	»	$339 + 71n$	$306.1 + 56.89n$	$224.4 + 41.702n$	$25.1 + 9.866n$		$n \geq 0$
$CaC_2O_4 \cdot nH_2O$	»	$328.4 + 71n$	$304.42 + 56.89n$	$223.13 + 41.702n$	$27.3 + 9.866n$	$25.4 + 10.99n$	$n \geq 0$
$tCaO \cdot mB_2O_3 \cdot nH_2O$	»	$166.8t + 318.1m + 71n$	$158.3t + 301.6m + 56.89n$	$116.18t + 221.06m + 41.702n$	$9.2t + 16.3m + 9.866n$	$9.7t + 15.68m + 10.99n$	$t > 0$ $m \geq 0$ $n \geq 0$

P. G. Maslov, "Thermodynamic Characteristics of Calcium, Gallium, Indium, and Thallium Compounds", Zhur. Obschei Khim., vol. 29, pp. 1413-23 (1959).

Landolt-Boernstein gives the value -421.0 Kcal/g mole for the heat of formation of $CaSO_3 \cdot 2H_2O$. This corresponds to the value -279 Kcal/ g mole given in Table III for anhydrous $CaSO_3$. This value was added to the TRACOR data file as an experimental value.

G. DISCUSSION AND RESULTS OBTAINED WITH MODIFIED ERDÖS METHOD

Of the above methods, two may be applied to our problem; the method of Wilcox and Bromley, and the method of Erdös.

First let us compare how well the two methods describe the heat of formation for sulfates and carbonates. Table IV & V summarizes the results of the previous sections.

Based on the above data the method of Erdös is the better one. Using the Erdös method, all literature values for sulfates, sulfites and carbonates have been correlated. The values of sulfates estimated by Wilcox and Bromley were included if experimental data on a particular cation were not available.

TABLE IV Maximum Deviation of Wilcox & Bromley & Erdös

Anion	Number of Compounds	Average Deviations (kcal/mole)	Max. Deviations kcal/mole Exp. - Calc.	Compounds of Maximum Deviations	Author
SO_4	25	± 1.95	6.10*	$CoSO_4$	Wilcox & Bromley
	17	± 1.5	+ 3.9	$PbSO_4$	Erdös
CO_3	17	± 1.23	3.53*	$MnCO_3$	Wilcox & Bromley
	17	± 1.6	- 3.9	$PbCO_3$	Erdös

*Wilcox and Bromley give no sign.

The deviation for $CoSO_4$ in Erdös' paper is (-3.1) and for $MnCO_3$, (+2.2). On the basis of this table, one can not decide which method is the best.

The predicted values for those cases where experimental results have been published since the correlations were published are given in Table V.

TABLE V

Deviations of Recently Published Data

Compound	Lit. Source	Lit. Value kcal/mole	Predicted by Wilcox & Bromley kcal/mole	Predicted by Erdös kcal/mole
Li_2SO_3	(12)	-279.4	-275	-278.3
$SrSO_3$	(13)	-279.4	-274	-279.7
$CdSO_3$	(12)	-163.9	-152	-164.4
$PbSO_3$	(13) (14)	-157.0 ± 0.1 and -161.1	-143	-157.6
$CaSO_3$	(15)	-279*	-273	-276.3

* (Calculated from value for $CaSO_3 \cdot 2H_2O$ with Maslov's relation.)

Table VI gives the results for the heats of reaction calculated by TRACOR using Erdös' method. The average deviation is ± 1.45 kcal/mole. The compounds in Table VII having the greatest deviations are given in Table VII.

TABLE VII

Maximum Deviations of TRACOR Correlation

$BaCO_3$	3.2 kcal/mole	$CoSO_4$	3.4 kcal/mole.
Cs_2CO_3	-3.3 kcal/mole.	$PbSO_4$	-3.0 kcal/mole.
$MgCO_3$	4.3 kcal/mole.	$NiSO_4$	-3.4 kcal/mole.
$MnCO_3$	-3.2 kcal/mole.		
$CoCO_3$	-5.0 kcal/mole.	$MgSO_3$	5.0 kcal/mole.
$NiCO_3$	5.0 kcal/mole.	Ag_2SO_3	-3.0 kcal/mole.
Ag_2CO_3	3.9 kcal/mole.		
$PbCO_3$	3.7 kcal/mole.		

TABLE VI

TRACOR CORRELATED AND ESTIMATED HEATS OF REACTION

HEAT OF REACTION, KCAL/GMOLE

COMPOUND	EXPERIMENTAL	CALCULATED	DIFFERENCE
LICO3	-5.376000+01	-5.222754+01	-1.532458+00
NACO3	-7.286000+01	-7.214609+01	-7.139111-01
KCO3	-9.152000+01	-9.294940+01	1.429399+00
RBCO3	-9.665000+01	-9.710058+01	4.505758-01
CSCO3	-1.045900+02	-1.012965+02	-3.293473+00
MGCO3	-2.636000+01	-2.202816+01	-4.331836+00
CACO3	-4.239000+01	-4.312313+01	7.331252-01
SRCO3	-5.625000+01	-5.474426+01	-1.505735+00
BACO3	-6.019000+01	-6.338202+01	3.192017+00
MN2CO3	-2.790000+01	-2.465174+01	-3.248255+00
FE2CO3	-2.079000+01	-1.972207+01	-1.067931+00
COCO3	-2.220000+01	-1.718145+01	-5.018550+00
NICO3	-1.166000+01	-1.665135+01	4.991347+00
CU2CO3	-8.600000+00	-1.053517+01	1.935174+00
AGCO3	-1.959000+01	-2.347606+01	3.886063+00
ZNCO3	-1.486000+01	-1.491629+01	5.629230-02
CDCO3	-2.327000+01	-2.216061+01	-1.109394+00
PB2CO3	-2.070000+01	-2.437318+01	3.673176+00
BECO3		-1.053367+01	
Y3CO3		-5.001090+01	
CE4CO3		-4.803150+01	
CE3CO3		-1.116049+02	
TI4CO3		-2.655417+01	
TI3CO3		-4.182696+01	
ZR4CO3		-5.421687+01	
V3CO3		-4.705973+01	
CR3CO3		-4.453169+01	
MN3CO3		-1.684031+01	
FE3CO3		-2.462312+01	
CU1CO3		-7.607762+00	
AL3CO3		-2.565319+01	
GA3CO3		-4.248438+01	
SN4CO3		-1.500233+00	
PB4CO3		-3.480422+01	
SB3CO3		-1.854877+01	
BI3CO3		-5.838428+01	
U3CO3		-3.643099+01	

```
  TH4CO3                      -3.848769+01
   PCCO3                      -2.128268+01
   LISO4    -1.056500+02      -1.072726+02       1.622638+00
   NASO4    -1.333400+02      -1.330564+02      -2.836514-01
    KSO4    -1.615600+02      -1.594793+02      -2.080652+00
   RBSO4    -1.669400+02      -1.647084+02      -2.231649+00
   CSSO4    -1.687300+02      -1.699817+02       1.251675+00
   MGSO4    -6.725000+01      -6.626828+01      -9.817209-01
   CASO4    -9.404000+01      -9.524241+01       1.202410+00
   SRSO4    -1.098100+02      -1.105662+02       7.561951-01
   BASO4    -1.225900+02      -1.217852+02      -8.048277-01
  MN2SO4    -6.770000+01      -6.999824+01       2.298245+00
  FE2SO4    -6.221000+01      -6.294419+01       7.341933-01
   COSO4    -5.583000+01      -5.922291+01       3.392908+00
   NISO4    -6.180000+01      -5.843744+01      -3.362558+00
  CU2SO4    -5.029000+01      -4.907154+01      -1.218461+00
   AGSO4    -6.864000+01      -6.833301+01      -3.069906-01
   ZNSO4    -5.588000+01      -5.584153+01      -3.846645-02
   CDSO4    -6.558000+01      -6.645782+01       8.778172-01
  PB2SO4    -7.260000+01      -6.960455+01      -2.995447+00
   BESO4    -4.907000+01      -4.906916+01      -8.444786-04
   Y3SO4    -1.754000+02      -1.753967+02      -3.255844-03
  CE4SO4    -1.382000+02      -1.381973+02      -2.738953-03
  CE3SO4    -2.619000+02      -2.618943+02      -5.699158-03
  TI4SO4    -1.067000+02      -1.066981+02      -1.906395-03
  TI3SO4    -1.631000+02      -1.630971+02      -2.943039-03
  ZR4SO4    -1.469000+02      -1.468970+02      -2.973557-03
   V3SO4    -1.710000+02      -1.709969+02      -3.135681-03
  CR3SO4    -1.672000+02      -1.671970+02      -3.034592-03
  MN3SO4    -1.226000+02      -1.225980+02      -1.950264-03
  FE3SO4    -1.359000+02      -1.358977+02      -2.267838-03
  CU1SO4    -4.430000+01      -4.429927+01      -7.290840-04
  AL3SO4    -1.376000+02      -1.375977+02      -2.296448-03
  GA3SO4    -1.641000+02      -1.640970+02      -2.962112-03
  SN4SO4    -6.180000+01      -6.179913+01      -8.659363-04
  PB4SO4    -1.191000+02      -1.190978+02      -2.227783-03
  SB3SO4    -1.256000+02      -1.255980+02      -2.018929-03
  BI3SO4    -1.877000+02      -1.876964+02      -3.578186-03
   U3SO4    -1.548000+02      -1.547973+02      -2.727509-03
  TH4SO4    -1.245000+02      -1.244976+02      -2.376556-03
   PDSO4    -6.520000+01      -6.519874+01      -1.262665-03
   LISO3    -6.600000+01      -6.545969+01      -5.401087-01
   NASO3    -8.660000+01      -8.756509+01       9.650927-01
```

```
     KSO3        -1.096000+02        -1.105611+02        9.610806-01
    RBSO3                            -1.151429+02
    CSSO3                            -1.197724+02
    MGSO3        -2.650000+01        -3.151807+01        5.018066+00
    CASO3        -5.740000+01        -5.530595+01       -2.094049+00
    SRSO3        -6.780000+01        -6.825995+01        4.599514-01
    BASO3        -7.980000+01        -7.785306+01       -1.946938+00
   MN2SO3                            -3.450908+01
   FE2SO3                            -2.887640+01
    COSO3                            -2.594916+01
    NISO3                            -2.533574+01
   CU2SO3                            -1.816456+01
    AGSO3        -3.620000+01        -3.317045+01       -3.029552+00
    ZNSO3                            -2.332048+01
    CDSO3        -3.180000+01        -3.166940+01       -1.306014-01
   PB2SO3        -3.370000+01        -3.419214+01        4.921393-01
    BESO3                            -1.816277+01
    Y3SO3                            -7.607308+01
   CE4SO3                            -6.757053+01
   CE3SO3                            -1.460252+02
   TI4SO3                            -4.280857+01
   TI3SO3                            -6.655057+01
   ZR4SO3                            -7.459685+01
    V3SO3                            -7.265000+01
   CR3SO3                            -6.970837+01
   MN3SO3                            -3.650481+01
   FE3SO3                            -4.610209+01
   CU1SO3                            -1.463674+01
   AL3SO3                            -4.735055+01
   GA3SO3                            -6.731918+01
   SN4SO3                            -1.096738+01
   PB4SO3                            -5.240842+01
   SB3SO3                            -3.864128+01
   BI3SO3                            -8.573093+01
    U3SO3                            -6.021295+01
   TH4SO3                            -5.665374+01
    PDSO3                            -3.066551+01

                          RMS = 1.448275+00
```

LITERATURE

1. Karapetjanc M. Ch.: Ž. fiz. chim. 30, 593 (1956)
2. Hoppe R: Z. anorgan. u. allgem. Chem. 296, 104 (1958)
3. Fomin V. V.: Ž. fiz. chim. 27, 1689 (1953)
4. Westland A. D.: Can. J. Chem. 37, 1451 (1959)
5. Erdös E.: Collection Czechoslov. Chem. Commun. 27, 1428 (1962)
6. Pauling L.: The Nature of the Chemical Bond
   Ithaca, New York
   Cornell University Press, 1960
7. H. W. Anderson and LeRoy A. Bromley: Journal of Physical Chemistry, Vol 63, (1959), pg. 1115 ff.
8. D. E. Wilcox, L. A. Bromley: "Heat and Free Energy of Formation for Simple Inorganic Compounds", Industrial and Engineering Chemistry, July 1963, pps. 32-39.
9. The background material with references to data source are available:
   Reprint Department
   A.C.S. Applied Publications
   1155 Sixteenth Street, N. W.
   Washington 6, D. C.
10. University of California, Lawrence Radiation Laboratory Report U.C.R.L., 10397
11. P. G. Maslov: "Thermodynamic Characteristics of Calcium, Gallium, Indium, and Thallium Compounds", Zhur. Obschceǐ Khim. 29, 1413-23 (1959)

12. Chem. Abstracts 64, 8996a

13. Chem. Abstracts 59, 13403g

14. NBS 270-2

15. Landolt-Börnstein

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

19 July 1968

004-009-02
P. S. Lowell
T. Parsons

TECHNICAL MEMORANDUM 004-009-Ch1A

ESTIMATION OF HEATS OF FORMATION

This memorandum describes in detail the computational method used for estimating heats of formation. The numerical results are included. The selection of this method over other methods was discussed in Technical Memorandum 004-009-Ch1

I. THEORY

It has been shown (Pa-1) that to a first approximation that the heat of formation may be calculated by summing the energy over all bonds. The arithmetic form of the first approximation is equation (1).

$$-\Delta H_f^\circ = \text{constant} \sum_{\substack{\text{over all}\\ \text{bonds}}} (X_A - X_B)^2 \qquad (1)$$

Erdös (Er-1) modified this method for two compounds reacting to form a third compound. He assumed that the majority of the chemical bonds of the reacting compounds are relatively undisturbed by the reaction. Hence all that need be estimated is the heat associated with the new bonds formed. This is the heat of reaction. Erdös did not use the quadratic form of equation (1), but rather let the exponent be an empirical constant. The form for the heat of reaction is given in equation (2).

$$-\Delta H^R_{ij} = B_{ij}(K_i - A_j)^{n_j} \tag{2}$$

The symbols are defined as follows:

i	$i^{\underline{th}}$ cation species
j	$j^{\underline{th}}$ anion species
K_i	Cation combining power
A_j	Anion combining power
n_j	Anion exponent
B_{ij}	Number of ion pair bonds formed
ΔH^R_{ij}	Heat of reaction of oxide containing $i^{\underline{th}}$ cation and acid containing $j^{\underline{th}}$ anion

For the reaction between a_{ij} moles of base with b_{ij} moles of acid to give one mole of compound, the heat of formation of the compound at 25° C is given by equation (3).

$$\Delta H^f_{ij} = a_{ij}\Delta H^f_i + b_{ij}\Delta H^f_j + \Delta H^R_{ij} \tag{3}$$

An example of this would be the heat of formation of $Fe_2(SO_4)_3$.

$$Fe_2O_3 + 3\ SO_3 \rightarrow Fe_2(SO_4)_3 \tag{4}$$

For this reaction Fe would be the cation represented by the subscript i (say i = 5 implies Fe). The anion $SO_4^=$ is represented by the subscript j (say j = 2). For this reaction $a_{ij} = 1$, $b_{ij} = 3$, and $B_{ij} = 3$.

The problem has two parts. The first part is the calculation of the K_i, A_j, and n_j's from existing data. The second part is the estimation of all possible compounds (combinations ij).

It is important that the data base be kept as internally consistent as possible. Hence it was decided to apply the Erdös method to the data in the TRACOR data base. This allowed inclusion of data not available to Erdös as well as keeping the data base internally consistent.

II. COMPUTATION METHOD

The computational scheme was to first correlate all available data. Next all remaining possibilities were estimated. The heats of reaction were first calculated and then correlated. Then heats of reaction for all remaining compounds were estimated. The estimated heats of reaction were added to the heats of formation of the reactants to give the estimated heat of formation of the compound. The $CO_3^=$ anion combining power (A_1) was arbitrarily set equal to zero.

The input information consists of a symbol representing a cation (e.g. Fe+2), the cation valence (+2 for Fe+2), the number of moles of cation available from its parent oxide base (1 for Fe+2), and the chemical formula of the parent base (FeO for Fe+2). The same information is given for "acid" compounds that will contribute the anions e.g. $CO_3^=$ and CO_2, $SO_4^=$ and SO_3, AlO_2^- and Al_2O_3, etc. The computer then calculates all stoichiometric coefficients a_{ij} and b_{ij} by determining the common factors of the valences. It also extracts the heat of formation of the compounds from the data base. Next the input data are given that relate cations, anions, and the resulting compound. For example Fe+3, $SO_4^=$, and $Fe_2(SO_4)_3$. With this information the computer associates Fe+3 with Fe_2O_3, $SO_4^=$ with SO_3, and looks up the heat of formation of $Fe_2(SO_4)_3$. Then with the stoichiometric coefficients, the heat of reaction and the number of ion bond pairs formed during the reaction are calculated. This is the information required to evaluate the coefficients in equation (2).

The coefficients in equation (2) are evaluated with a least squares technique. Let the difference between the observed and calculated values be Δ_{ij}. Let $E_{ij}=1$ if the data for compound ij are entered into the correlation. $E_{ij}=0$ if the data are not entered into the correlation. The error for two ionic bonds is then minimized (thus Li_2O and Fe_2O_3 are given the same weight). The squared error is given on the next page.

$$\sum_{\substack{\text{all compounds}\\ \text{with data}}} \Delta_{ij}^2 = \sum_{i}\sum_{j} E_{ij} \left[\Delta H_{ij}/B_{ij} + (K_i - A_j)^{n_j} \right]^2 \qquad (5)$$

This expression has a minimum when-

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial K_i} = 0 \qquad (6a)$$

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial A_j} = 0 \qquad (6b)$$

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial n_j} = 0 \qquad (6c)$$

Performing the indicated differentiations gives the following set of equations for a total I cations and J anions:

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial K_i} = 2 \sum_{j} E_{ij} \left[\Delta H_{ij}/B_{ij} + (K_i - A_j)^{n_j} \right] n_j (K_i - A_j)^{n_j - 1} \qquad (7a)$$

$$= 0 \qquad \text{for } i = 1 \text{ to } I$$

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial A_j} = -2\sum_i E_{ij}[\Delta H_{ij}/B_{ij}+(K_i-A_j)^{n_j}]n_j(K_i-A_j)^{n_j-1} \qquad (7b)$$

$$= 0 \qquad \text{for } j = 2 \text{ to } J$$

$$\frac{\partial \Sigma \Delta_{ij}^2}{\partial n_j} = 2\sum_i E_{ij}[\Delta H_{ij}+(K_i-A_j)^{n_j}](K_i-A_j)^{n_j} \ln(K_i-A_j) \qquad (7c)$$

$$= 0 \qquad \text{for } j = 1 \text{ to } J$$

A steepest descent technique was used. This will be given in limited detail below. Let our function be:

$$f = \sum_{ij}\sum \Delta_{ij}^2 = f_{(x_1, x_2, \cdots)} \qquad (8)$$

This has a minimum at:

$$\frac{\partial f}{\partial x_1} = \frac{\partial f}{\partial x_2} = \cdots = 0 \qquad (9)$$

This is the same criterion as Equation 7a, b, and c. We now form this criterion in a positive definite form with a φ function:

$$\varphi = \sum_i \left(\frac{\partial f}{\partial x_i}\right)^2 \tag{10}$$

If φ is zero, then all of the partials must be zero.

An initial estimate is made of the x_i's. This initial estimate is corrected with a modified Newton-Raphson technique based on the gradient. If the m$^{\underline{th}}$ correction of the initial guess was $\varphi^m(x_1^m, x_2^m, \cdots)$ then the m+1$^{\underline{th}}$ correction would be calculated as follows:

$$\varphi^{m+1} = \varphi^m + \Delta\varphi^m = 0 \tag{11}$$

The value for $\Delta\varphi^m$ (neglecting higher order terms) is:

$$\Delta\varphi^m = \sum_i \Delta x_i^m \frac{\partial\varphi^m}{\partial X_i} = \vec{\Delta x}^m \cdot \nabla\varphi^m \tag{12}$$

The correction vector $\vec{\Delta x}$ has both magnitude and direction. We require that the direction be that causing the steepest descent of φ^m, i.e., the direction of $\nabla\varphi^m$.

If the magnitude of the correction vector is α, $\vec{\Delta x}$ may be expressed as follows:

$$\vec{\Delta x}^m = \alpha \frac{\nabla\varphi^m}{|\nabla\varphi|} \tag{13}$$

Substituting 13 into 12 and 11 yields:

$$\alpha \frac{\nabla\varphi^m}{|\nabla\varphi^m|} \cdot \nabla\varphi^m = \alpha |\nabla\varphi^m| = -\varphi^m \qquad (14)$$

Substituting 14 into 13:

$$\Delta\vec{x}^m = \frac{-\varphi^m}{|\nabla\varphi^m|} \; \frac{\nabla\varphi^m}{|\nabla\varphi^m|} \qquad (15)$$

For the individual components:

$$x_i^{m+1} = x_i^m - \frac{\varphi^m}{|\nabla\varphi^m|^2} \; \frac{\partial\varphi^m}{\partial x_i} \qquad (16)$$

In actual practice it was found that the scale of variation for coefficients of the K_i and A_j type were markedly different from the scale of the n_j type. Hence the solution was converged by assuming the n_j's constant and iterating on the K_i's and A_j's. Next the K_i's and A_j's were held constant and the n_j's iterated. This process was continued until a solution was obtained.

After the K_i's, A_j's, and n_j's were calculated the heats of reaction of all possible ij combinations were calculated. Where data were put into the program the error between estimated and observed quantities was calculated. The root mean square error was also calculated as an estimate of the accuracy of the correlation.

$$\text{RMS Error} = \left\{ \frac{\sum\limits_{i}\sum\limits_{j} E_{ij}\left[\Delta H_{ij}/B_{ij} + (K_i - A_j)^{n_j}\right]^2}{\sum\limits_{i}\sum\limits_{j} E_{ij}} \right\}^{\frac{1}{2}} \qquad (17)$$

III. RESULTS

Using the method discussed in Section II, the heats of formation of the sulfites, titanates, aluminates, chromates, ferrates, vanadates, wolframates, and molybdates for thirty cations were estimated from the heats of formation of their sulfates and carbonates. The resulting heats of formation are included in this report, along with the K_i, A_j, and n_j values for the cations and anions and the heats of formation of the constituent oxides from the TRACOR data base.

The correlation consisted of the calculation of A_j, K_i, and n_j values from existing data and the subsequent comparison of heats of formation predicted by these A_j, K_i, and n_j vlaues with existing data. The comparison of predicted and experimentally obtained values is described by the RMS (Root Mean Square) of the deviations.

Since the K_i value for a particular cation is dependent on the heats of formation of all the compounds in which the cation occurs, the heat of formation of a particular compound may be estimated just from the heats of formation of the sulfates and carbonates, or from the heats of formation of other compounds having the same cation or anion. For instance, the heat of formation of $Na_2Al_2O_4$ may be estimated from Na_2SO_4 and Na_2CO_3 and other aluminate data alone, or data for Na_2TiO_3 or $Na_2Fe_2O_4$ may be used in the correlation as well.

In Technical Memorandum 004-009-Ch5, which describes the selection and implementation of a method for estimating absolute entropy, methods of statistical analyses were applied in determining the comparative accuracy for two methods of grouping data. Using the same methods it was found that more accurate results were obtained when data for all the compounds of a particular cation were used in the correlation, rather than just carbonate and sulfate data. (See Table I.)

After the most accurate method of grouping data for the correlation was determined, unknown heats of formation were estimated using the K_i, A_j, and n_j values from the correlation. The results are shown in Table II. Figure I shows K_i, the cation combining power, as a function of the position of the cation in the periodic table.

The RMS Error for the estimation method is three kilocalories. An error of this magnitude is reasonable since different literature values for the heat of formation of a particular mixed oxide may be as much as 10 kilocalories apart. When only one value for a mixed oxide heat of formation was reported, and if the value was

TABLE I

ANALYSIS OF ERRORS INVOLVED IN METHODS OF DATA GROUPING

GROUP	N*	RMS**	$\frac{(RMS)^2 N^2}{N-1}$
Carbonates, Sulfates, and Aluminates	25	3.55	327.9
Carbonates, Sulfates, Wolframates, and Molybdates	30	5.42	909.1
Carbonates, Sulfates*, and Ferrates	17	3.15	179.0
Carbonates, Sulfates, Chromates, and Vanadates	17	2.67	128.3
Carbonates, Sulfates, Sulfites, and Titanates	42	2.63	282.8
All Anions	80	4.65	1738.7

$$\sum_{\text{All Groups}} \frac{(RMS)^2 N^2}{N-1} = 1827.1$$

* Number of data points

** Root Mean Square of the deviation

TABLE II

COMPUTER INPUT AND OUTPUT DATA

I. DETERMINATION OF ACCURACY OF GROUPING METHOD

A. SMALL GROUPS OF ANIONS

1. Carbonates and Sulfates
2. Sulfites and Titanates
3. Chromates and Vanadates
4. Ferrates
5. Wolframates and Molybdates
6. Aluminates

B. LARGE GROUP OF ALL ANIONS

II. ESTIMATION OF UNKNOWN HEATS

TABLE II (continued)

COMPUTER INPUT AND OUTPUT DATA

I. DETERMINATION OF ACCURACY OF GROUPING METHOD

A. SMALL GROUPS OF ANIONS

1. Carbonates and Sulfates
2. Sulfites and Titanates
3. Chromates and Vanadates
4. Ferrates
5. Wolframates and Molybdates
6. Aluminates

```
                                   INPUT DATA

           CATIONS = 30          ANIONS =  2          DATA POINTS = 47

                                                    CATIONS PER         CATION
  CATION NO.         CATION        METAL OXIDE      METAL OXIDE        VALENCE
     (I)             CEF(I)                           CIPO(I)           CIV(I)

      1                AG            AG2O                2                 1
      2               AL3            AL2O3               2                 3
      3                BA            BAO                 1                 2
      4                BE            BEO                 1                 2
      5               BI3            BI2O3               2                 3
      6                CA            CAO                 1                 2
      7                CD            CDO                 1                 2
      8               CE4            CEO2                1                 4
      9                CO            COO                 1                 2
     10               CS1            CS2O                2                 1
     11               CU2            CUO                 1                 2
     12               CU1            CU2O                2                 1
     13               FE2            FEO                 1                 2
     14               FE3            FE2O3               2                 3
     15                 K            K2O                 2                 1
     16                LI            LI2O                2                 1
     17                MG            MGO                 1                 2
     18               MN2            MNO                 1                 2
     19               MN3            MN2O3               2                 3
     20                NA            NA2O                2                 1
     21                NI            NIO                 1                 2
     22               PB2            PBO                 1                 2
     23               RB1            RB2O                2                 1
     24               SB3            SB2O3               2                 3
     25               SN4            SNO2                1                 4
     26                SR            SRO                 1                 2
     27               TH4            THO2                1                 4
     28                U4            UO2                 1                 4
     29                ZN            ZNO                 1                 2
     30               ZR4            ZRO2                1                 4

                                                    ANIONS PER          ANION
```

```
ANION NO.        ANION        ANION ACID      MOLE ACID      VALENCE
  (J)            AEF(J)                       AIPM(J)         AIV(J)

   1              CO3            CO2             1              2
   2              SO4            SO3             1              2
```

```
                              OUTPUT DATA

    ION               ION VALUE               EXP VALUE

     AG               8.5865+00
    AL3               4.3369+00
     BA               1.7999+01
     BE               4.9655+00
    BI3               7.6982+00
     CA               1.3503+01
     CD               8.5229+00
    CE4               8.9593+00
     CO               7.8162+00
    CS1               [illegible]
    CU2               5.0769+00
    CU1               4.0373+00
    FE2               7.8600+00
    FE3               4.2519+00
      K               2.3725+01
     LI               1.5649+01
     MG               9.0333+00
    MN2               9.1813+00
    MN3               5.0387+00
     NA               1.9828+01
     NI               6.9947+00
    PB2               9.1907+00
    RB1               2.4552+01
    SB3               3.2570+00
    SN4               1.2564+00
     SR               1.6269+01
    TH4               7.6773+00
     U4               6.6112+00
     ZN               6.5896+00
    ZR4               9.8710+00

    CO3               0.0000                  1.4335+00
    SO4              -9.8323+00               1.4441+00
```

```
                         HEAT OF FORMATION AT 25 DEG C
                            CALORIES/GRAM MOLE

    COMPOUND          I   J     PAIRS OF                      HEAT OF FORMATION
                                IONIC BONDS      CALCULATED        ACTUAL            ERROR

(   AG)2(   CO3)      1   1        1.0           -1.2312+02    -1.2088+02       2.2358+00
(  AL3)2(   CO3)3     2   1        3.0           -7.0676+02
(   BA) (   CO3)      3   1        1.0           -2.8909+02    -2.8716+02       1.9337+00
(   BE) (   CO3)      4   1        1.0           -2.4699+02
(  BI3)2(   CO3)3     5   1        3.0           -4.7606+02
(   CA) (   CO3)      6   1        1.0           -2.8747+02    -2.8811+02      -6.4464-01
(   CD) (   CO3)      7   1        1.0           -1.7677+02    -1.7846+02      -1.6886+00
(  CE4) (   CO3)2     8   1        2.0           -4.6730+02
(   CO) (   CO3)      9   1        1.0           -1.7014+02    -1.7331+02      -3.1673+00
(  CS1)2(   CO3)     10   1        1.0           -2.7078+02    -2.7447+02      -3.6931+00
(  CU2) (   CO3)     11   1        1.0           -1.4377+02    -1.4210+02       1.6698+00
(  CU1)2(   CO3)     12   1        1.0           -1.4218+02
(  FE2) (   CO3)     13   1        1.0           -1.7699+02    -1.7855+02      -1.5687+00
(  FE3)2(   CO3)3    14   1        3.0           -5.0234+02
(    K)2(   CO3)     15   1        1.0           -2.7400+02    -2.7187+02       2.1270+00
(   LI)2(   CO3)     16   1        1.0           -2.8807+02    -2.9026+02      -2.1925+00
(   MG) (   CO3)     17   1        1.0           -2.6109+02    -2.6398+02      -2.8944+00
(  MN2) (   CO3)     18   1        1.0           -2.0995+02    -2.1374+02      -3.7988+00
(  MN3)2(   CO3)3    19   1        3.0           -5.4161+02
(   NA)2(   CO3)     20   1        1.0           -2.6927+02    -2.6972+02      -4.5160-01
(   NI) (   CO3)     21   1        1.0           -1.6753+02    -1.6298+02       4.5511+00
(  PB2) (   CO3)     22   1        1.0           -1.7042+02    -1.6723+02       3.1886+00
(  RB1)2(   CO3)     23   1        1.0           -2.7118+02    -2.6948+02       1.7037+00
(  SB3)2(   CO3)3    24   1        3.0           -4.6823+02
(  SN4) (   CO3)2    25   1        2.0           -3.2955+02
(   SR) (   CO3)     26   1        1.0           -2.8926+02    -2.9098+02      -1.7216+00
(  TH4) (   CO3)2    27   1        2.0           -5.1926+02
(   U4) (   CO3)2    28   1        2.0           -4.7697+02
(   ZN) (   CO3)     29   1        1.0           -1.9231+02    -1.9368+02      -1.3680+00
(  ZR4) (   CO3)2    30   1        2.0           -5.0264+02


(   AG)2(   SO4)      1   2        1.0           -1.6888+02    -1.7036+02      -1.4763+00
(  AL3)2(   SO4)3     2   2        3.0           -8.2137+02    -8.2038+02       9.8532-01
(   BA) (   SO4)      3   2        1.0           -3.4840+02    -3.4999+02      -1.5884+00
(   BE) (   SO4)       4   2        1.0           -2.8641+02     -2.8565+02      7.5786-01
(  BI3)2(   SO4)3      5   2        3.0           -6.0895+02     -6.0810+02      8.4979-01
(   CA) (   SO4)       6   2        1.0           -3.4067+02     -3.4019+02      4.7286-01
(   CD) (   SO4)       7   2        1.0           -2.2243+02     -2.2120+02      1.2329+00
(  CE4) (   SO4)2      8   2        2.0           -5.6004+02     -5.6000+02      3.6545-02
(   CO) (   SO4)       9   2        1.0           -2.1464+02
(  CS1)2(   SO4)      10   2        1.0           -3.3884+02     -3.3900+02     -1.6265-01
(  CU2) (   SO4)      11   2        1.0           -1.8340+02     -1.8422+02     -8.1401-01
(  CU1)2(   SO4)      12   2        1.0           -1.7979+02     -1.7951+02      2.7630-01
(  FE2) (   SO4)      13   2        1.0           -2.2155+02     -2.2041+02      1.1438+00
(  FE3)2(   SO4)3     14   2        3.0           -6.1644+02     -6.1560+02      8.4064-01
(    K)2(   SO4)      15   2        1.0           -3.4051+02     -3.4234+02     -1.8308+00
(   LI)2(   SO4)      16   2        1.0           -3.4425+02     -3.4258+02      1.6650+00
(   MG) (   SO4)      17   2        1.0           -3.0757+02     -3.0550+02      2.0748+00
(  MN2) (   SO4)      18   2        1.0           -2.5667+02     -2.5395+02      2.7165+00
(  MN3)2(   SO4)3     19   2        3.0           -6.6029+02     -6.6690+02     -6.6082+00
(   NA)2(   SO4)      20   2        1.0           -3.3094+02     -3.3064+02      2.9771-01
(   NI) (   SO4)      21   2        1.0           -2.1063+02     -2.1350+02     -2.8775+00
(  PB2) (   SO4)      22   2        1.0           -2.1715+02     -2.1933+02     -2.1793+00
(  RB1)2(   SO4)      23   2        1.0           -3.3870+02     -3.4019+02     -1.4904+00
(  SB3)2(   SO4)3     24   2        3.0           -5.7619+02     -5.7420+02      1.9856+00
(  SN4) (   SO4)2     25   2        2.0           -3.9214+02     -3.9340+02     -1.2626+00
(   SR) (   SO4)      26   2        1.0           -3.4627+02     -3.4497+02      1.3026+00
(  TH4) (   SO4)2     27   2        2.0           -6.0778+02     -6.0726+02      5.2101-01
(   U4) (   SO4)2     28   2        2.0           -5.6183+02     -5.6300+02     -1.1666+00
(   ZN) (   SO4)      29   2        1.0           -2.3470+02     -2.3369+02      1.0089+00
(  ZR4) (   SO4)2     30   2        2.0           -5.9826+02     -5.9701+02      1.2472+00


              ROOT MEAN SQUARE ERROR =  1.8656+00    CALORIES/PAIR OF IONIC BONDS
```

```
                                   INPUT DATA

              CATIONS = 14          ANIONS =  4          DATA POINTS = 42

                                                      CATIONS PER         CATION
CATION NO.         CATION          METAL OXIDE        METAL OXIDE         VALENCE
   (I)             CEF(I)                              CIPO(I)            CIV(I)

    1                AG               AG2O             2.000+00              1
    2                BA               BAO              1.000+00              2
    3                CA               CAO              1.000+00              2
    4                CD               CDO              1.000+00              2
    5                CO               COO              1.000+00              2
    6                 K               K2O              2.000+00              1
    7                LI               LI2O             2.000+00              1
    8                MG               MGO              1.000+00              2
    9              MN+2               MNO              1.000+00              2
   10                NA               NA2O             2.000+00              1
   11                NI               NIO              1.000+00              2
   12                PB               PBO              1.000+00              2
   13                SR               SRO              1.000+00              2
   14                ZN               ZNO              1.000+00              2

                                                      ANIONS PER          ANION
ANION NO.          ANION           ANION ACID          MOLE ACID          VALENCE
   (J)             AEF(J)                               AIPM(J)           AIV(J)

    1               CO3               CO2              1.000+00              2
    2               SO4               SO3              1.000+00              2
    3               SO3               SO2              1.000+00              2
    4              TIO3               TIO2             1.000+00              2
```

```
                              OUTPUT DATA

       ION                    ION VALUE                    EXP VALUE

        AG                     8.9976+00
        BA                     1.8450+01
        CA                     1.3656+01
        CD                     8.6362+00
        CO                     9.0102+00
         K                     2.4164+01
        LI                     1.5970+01
        MG                     8.5252+00
      MN+2                     9.3016+00
        NA                     2.0145+01
        NI                     7.3555+00
        PB                     9.2624+00
        SR                     1.7198+01
        ZN                     6.7684+00

       CO3                     0.0000                      1.4217+00
       SO4                    -9.4967+00                   1.4442+00
       SO3                    -3.1265+00                   1.4218+00
      TIO3                     5.4393+00                   1.3999+00
```

```
                              HEAT OF FORMATION AT 25 DEG C
                                  CALORIES/GRAM MOLE

    COMPOUND          I   J      PAIRS OF                        HEAT OF FORMATION
                                IONIC BONDS       CALCULATED          ACTUAL           ERROR

 (   AG)2(   CO3)     1   1         1.0           -1.2403+02       -1.2088+02       3.1505+00
 (   BA) (   CO3)     2   1         1.0           -2.8916+02       -2.8716+02       1.9998+00
 (   CA) (   CO3)     3   1         1.0           -2.8686+02       -2.8811+02      -1.2574+00
 (   CD) (   CO3)     4   1         1.0           -1.7663+02       -1.7846+02      -1.8298+00
 (   CO) (   CO3)     5   1         1.0           -1.7385+02       -1.7331+02       5.4124-01
 (    K)2(   CO3)     6   1         1.0           -2.7294+02       -2.7187+02       1.0692+00
 (   LI)2(   CO3)     7   1         1.0           -2.8788+02       -2.9026+02      -2.3801+00
 (   MG) (   CO3)     8   1         1.0           -2.5868+02       -2.6398+02      -5.3020+00
 ( MN+2) (   CO3)     9   1         1.0           -2.0976+02       -2.1374+02      -3.9831+00
 (   NA)2(   CO3)    10   1         1.0           -2.6835+02       -2.6972+02      -1.3695+00
 (   NI) (   CO3)    11   1         1.0           -1.6834+02       -1.6298+02       5.3591+00
 (   PB) (   CO3)    12   1         1.0           -1.7006+02       -1.6723+02       2.8263+00
 (   SR) (   CO3)    13   1         1.0           -2.9182+02       -2.9098+02       8.4427-01
 (   ZN) (   CO3)    14   1         1.0           -1.9255+02       -1.9368+02      -1.1308+00

 (   AG)2(   SO4)     1   2         1.0           -1.6930+02       -1.7036+02      -1.0574+00
 (   BA) (   SO4)     2   2         1.0           -3.4918+02       -3.4999+02      -8.1329-01
 (   CA) (   SO4)     3   2         1.0           -3.3963+02       -3.4019+02      -5.6559-01
 (   CD) (   SO4)     4   2         1.0           -2.2128+02       -2.2120+02       8.6550-02
 (   CO) (   SO4)     5   2         1.0           -2.1914+02
 (    K)2(   SO4)     6   2         1.0           -3.4128+02       -3.4234+02      -1.0611+00
 (   LI)2(   SO4)     7   2         1.0           -3.4419+02       -3.4258+02       1.6119+00
 (   MG) (   SO4)     8   2         1.0           -3.0315+02       -3.0550+02      -2.3512+00
 ( MN+2) (   SO4)     9   2         1.0           -2.5554+02       -2.5395+02       1.5892+00
 (   NA)2(   SO4)    10   2         1.0           -3.3086+02       -3.3064+02       2.2319-01
 (   NI) (   SO4)    11   2         1.0           -2.1077+02       -2.1350+02      -2.7327+00
 (   PB) (   SO4)    12   2         1.0           -2.1577+02       -2.1933+02      -3.5642+00
 (   SR) (   SO4)    13   2         1.0           -3.4998+02       -3.4497+02       5.0095+00
 (   ZN) (   SO4)    14   2         1.0           -2.3393+02       -2.3369+02       2.4205-01

 (   AG)2(   SO3)     1   3         1.0           -1.1296+02       -1.1440+02      -1.4355+00
 (   BA) (   SO3)     2   3         1.0           -2.8183+02       -2.8260+02      -7.6888-01
 (   CA) (   SO3)     3   3         1.0           -2.7780+02       -2.7588+02       1.9193+00
```

```
(    CD)  (   SO3)        4    3          1.0           -1.6538+02      -1.6390+02        1.4828+00
(    CO)  (   SO3)        5    3          1.0           -1.6279+02
(     K)2(    SO3)        6    3          1.0           -2.6739+02      -2.6690+02        4.8527-01
(    LI)2(    SO3)        7    3          1.0           -2.7970+02      -2.7940+02        2.9649-01
(    MG)  (   SO3)        8    3          1.0           -2.4738+02      -2.4100+02        6.3819+00
(  MN+2)  (   SO3)        9    3          1.0           -1.9884+02      -1.9737+02        1.4669+00
(    NA)2(    SO3)       10    3          1.0           -2.6158+02      -2.6040+02        1.1745+00
(    NI)  (   SO3)       11    3          1.0           -1.5644+02
(    PB)  (   SO3)       12    3          1.0           -1.5911+02      -1.5700+02        2.1138+00
(    SR)  (   SO3)       13    3          1.0           -2.8407+02      -2.9098+02       -6.9083+00
(    ZN)  (   SO3)       14    3          1.0           -1.8032+02

(    AG)2(   TIO3)        1    4          1.0           -2.3871+02
(    BA)  (  TIO3)        2    4          1.0           -3.9387+02
(    CA)  (  TIO3)        3    4          1.0           -3.9630+02
(    CD)  (  TIO3)        4    4          1.0           -2.9177+02
(    CO)  (  TIO3)        5    4          1.0           -2.8851+02      -2.8946+02       -9.4864-01
(     K)2(   TIO3)        6    4          1.0           -3.7229+02
(    LI)2(   TIO3)        7    4          1.0           -3.9500+02
(    MG)  (  TIO3)        8    4          1.0           -3.7397+02      -3.7150+02        2.4670+00
(  MN+2)  (  TIO3)        9    4          1.0           -3.2406+02
(    NA)2(   TIO3)       10    4          1.0           -3.7145+02
(    NI)  (  TIO3)       11    4          1.0           -2.8525+02      -2.8775+02       -2.5027+00
(    PB)  (  TIO3)       12    4          1.0           -2.8440+02
(    SR)  (  TIO3)       13    4          1.0           -3.9774+02
(    ZN)  (  TIO3)       14    4          1.0           -3.1036+02      -3.0927+02        1.0931+00


          ROOT MEAN SQUARE ERROR =   2.6255+00     CALORIES/PAIR OF IONIC BONDS
```

```
                              INPUT DATA

          CATIONS =  5          ANIONS =  4          DATA POINTS = 17

                                                 CATIONS PER        CATION
CATION NO.        CATION       METAL OXIDE       METAL OXIDE       VALENCE
   (I)            CEF(I)                           CIPO(I)          CIV(I)

    1                 AG          AG2O            2.000+00             1
    2                 CA          CAO             1.000+00             2
    3                 MG          MGO             1.000+00             2
    4                 NA          NA2O            2.000+00             1
    5               PB+2          PBO             1.000+00             2

                                                 ANIONS PER         ANION
ANION NO.         ANION        ANION ACID         MOLE ACID        VALENCE
   (J)            AEF(J)                           AIPM(J)          AIV(J)

    1                CO3          CO2             1.000+00             2
    2                SO4          SO3             1.000+00             2
    3               CRO4          CRO3            1.000+00             2
    4               V2O6          V2O5            1.000+00             2
```

```
                         OUTPUT DATA

         ION             ION VALUE           EXP VALUE

          AG              9.0414+00
          CA              1.3588+01
          MG              8.9112+00
          NA              2.0941+01
        PB+2              9.5231+00

         CO3              0.0000              1.4128+00
         SO4             -9.6205+00           1.4382+00
        CRO4              2.1729-01           1.4128+00
        V2O6              2.1062+00           1.4740+00
```

```
                         HEAT OF FORMATION AT 25 DEG C
                              CALORIES/GRAM MOLE

   COMPOUND         I  J    PAIRS OF                        HEAT OF FORMATION
                           IONIC BONDS      CALCULATED           ACTUAL           ERROR

(   AG)2(  CO3)     1  1       1.0          -1.2375+02        -1.2088+02       2.8640+00
(   CA) (  CO3)     2  1       1.0          -2.8563+02        -2.8811+02      -2.4849+00
(   MG) (  CO3)     3  1       1.0          -2.5962+02        -2.6398+02      -4.3663+00
(   NA)2(  CO3)     4  1       1.0          -2.7038+02        -2.6972+02       6.6218-01
( PB+2) (  CO3)     5  1       1.0          -1.7052+02        -1.6723+02       3.2906+00

(   AG)2(  SO4)     1  2       1.0          -1.6899+02        -1.7036+02      -1.3711+00
(   CA) (  SO4)     2  2       1.0          -3.3819+02        -3.4019+02      -2.0052+00
(   MG) (  SO4)     3  2       1.0          -3.0464+02        -3.0550+02      -8.5971-01
(   NA)2(  SO4)     4  2       1.0          -3.3403+02        -3.3064+02       3.3953+00
( PB+2) (  SO4)     5  2       1.0          -2.1657+02        -2.1933+02      -2.7683+00

(   AG)2( CRO4)     1  3       1.0          -1.7100+02        -1.7237+02      -1.3661+00
(   CA) ( CRO4)     2  3       1.0          -3.3274+02        -3.2944+02       3.2993+00
(   MG) ( CRO4)     3  3       1.0          -3.0688+02
(   NA)2( CRO4)     4  3       1.0          -3.1731+02        -3.1860+02      -1.2877+00
( PB+2) ( CRO4)     5  3       1.0          -2.1776+02        -2.1750+02       2.6030-01

(   AG)2( V2O6)     1  4       1.0          -3.9735+02
(   CA) ( V2O6)     2  4       1.0          -5.6092+02        -5.5870+02       2.2182+00
(   MG) ( V2O6)     3  4       1.0          -5.3320+02        -5.2790+02       5.2979+00
(   NA)2( V2O6)     4  4       1.0          -5.5128+02        -5.5294+02      -1.6615+00
( PB+2) ( V2O6)     5  4       1.0          -4.4422+02


          ROOT MEAN SQUARE ERROR =  2.6653+00    CALORIES/PAIR OF IONIC BONDS
```

```
                              INPUT DATA

          CATIONS =  6          ANIONS =  3          DATA POINTS = 17

                                                   CATIONS PER        CATION
CATION NO.         CATION        METAL OXIDE       METAL OXIDE        VALENCE
   (I)             CEF(I)                            CIPO(I)          CIV(I)

    1                 BA            BAO            1.000+00             2
    2               CU+2            CUO            1.000+00             2
    3                 LI            LI20           2.000+00             1
    4                 MG            MGO            1.000+00             2
    5               MN+2            MNO            1.000+00             2
    6                 NI            NIO            1.000+00             2

                                                    ANIONS PER        ANION
ANION NO.          ANION         ANION ACID         MOLE ACID         VALENCE
   (J)             AEF(J)                            AIPM(J)          AIV(J)

    1                C03            C02             1.000+00            2
    2                S04            S03             1.000+00            2
    3              FE204            FE203           1.000+00            2
```

```
                         OUTPUT DATA

        ION              ION VALUE           EXP VALUE

         BA               1.6303+01
       CU+2               4.1221+00
         LI               1.3940+01
         MG               8.2759+00
       MN+2               9.3256+00
         NI               6.2012+00

        CO3               0.0000              1.4890+00
        SO4              -1.0099+01           1.4674+00
      FE2O4               6.1749+00           1.2961+00
```

```
                         HEAT OF FORMATION AT 25 DEG C
                              CALORIES/GRAM MOLE

    COMPOUND          I   J     PAIRS OF                      HEAT OF FORMATION
                              IONIC BONDS      CALCULATED          ACTUAL            ERROR

(   BA) (   CO3)      1   1       1.0          -2.8992+02      -2.8716+02        2.7631+00
( CU+2) (   CO3)      2   1       1.0          -1.4174+02      -1.4210+02       -3.5805-01
(    LI)2(  CO3)      3   1       1.0          -2.8708+02      -2.9026+02       -3.1861+00
(   MG) (   CO3)      4   1       1.0          -2.6090+02      -2.6398+02       -3.0864+00
( MN+2) (   CO3)      5   1       1.0          -2.1373+02      -2.1374+02       -1.6861-02
(   NI) (   CO3)      6   1       1.0          -1.6641+02      -1.6298+02        3.4325+00

(   BA) (   SO4)      1   2       1.0          -3.4840+02      -3.4999+02       -1.5916+00
( CU+2) (   SO4)      2   2       1.0          -1.8308+02      -1.8422+02       -1.1353+00
(    LI)2(  SO4)      3   2       1.0          -3.4316+02      -3.4258+02        5.7789-01
(   MG) (   SO4)      4   2       1.0          -3.0967+02      -3.0550+02        4.1654+00
( MN+2) (   SO4)      5   2       1.0          -2.6405+02
(   NI) (   SO4)      6   2       1.0          -2.1176+02      -2.1350+02       -1.7487+00

(   BA) (FE2O4)       1   3       1.0          -3.4860+02      -3.5049+02       -1.8896+00
( CU+2) (FE2O4)       2   3       1.0          -2.3337+02      -2.3751+02       -4.1363+00
(    LI)2(FE2O4)      3   3       1.0          -3.5318+02      -3.4740+02        5.7754+00
(   MG) (FE2O4)       4   3       1.0          -3.4267+02      -3.4922+02       -6.5522+00
( MN+2) (FE2O4)       5   3       1.0          -2.9278+02      -2.9300+02       -2.2191-01
(   NI) (FE2O4)       6   3       1.0          -2.5370+02      -2.5646+02       -2.7631+00


          ROOT MEAN SQUARE ERROR =  3.1477+00     CALORIES/PAIR OF IONIC BONDS
```

```
                                 INPUT DATA

              CATIONS =  9           ANIONS =  4          DATA POINTS = 30

                                                          CATIONS PER       CATION
     CATION NO.          CATION          METAL OXIDE      METAL OXIDE      VALENCE
        (I)              CEF(I)                             CIPO(I)         CIV(I)

         1                 AG               AG20           2.000+00           1
         2                 BA               BAO            1.000+00           2
         3                 MG               MGO            1.000+00           2
         4               MN+2               MNO            1.000+00           2
         5                 NA               NA20           2.000+00           1
         6               PB+2               PBO            1.000+00           2
         7                 NI               NIO            1.000+00           2
         8                 SR               SRO            1.000+00           2
         9                 ZN               ZNO            1.000+00           2

                                                          ANIONS PER        ANION
     ANION NO.           ANION           ANION ACID        MOLE ACID       VALENCE
        (J)              AEF(J)                             AIPM(J)         AIV(J)

         1                CO3               CO2            1.000+00           2
         2                SO4               SO3            1.000+00           2
         3                WO4               WO3            1.000+00           2
         4               MOO4               MOO3           1.000+00           2
```

```
                              OUTPUT DATA

   ION                        ION VALUE            EXP VALUE

    AG                         8.9298+00
    BA                         1.8694+01
    MG                         9.3575+00
  MN+2                         8.2322+00
    NA                         2.0295+01
  PB+2                         9.9856+00
    NI                         6.7578+00
    SR                         1.6156+01
    ZN                         8.5007+00

   CO3                         0.0000                1.4198+00
   SO4                        -9.2558+00             1.4479+00
   WO4                        -1.3715+00             1.4127+00
  MOO4                        -1.4518+00             1.3982+00
```

```
                       HEAT OF FORMATION AT 25 DEG C
                          CALORIES/GRAM MOLE

   COMPOUND          I   J     PAIRS OF                     HEAT OF FORMATION
                              IONIC BONDS     CALCULATED       ACTUAL          ERROR

(   AG)2(   CO3)     1   1       1.0          -1.2370+02     -1.2088+02     2.8161+00
(   BA) (   CO3)     2   1       1.0          -2.9000+02     -2.8716+02     2.8425+00
(   MG) (   CO3)     3   1       1.0          -2.6156+02     -2.6398+02    -2.4215+00
( MN+2) (   CO3)     4   1       1.0          -2.0589+02     -2.1374+02    -7.8584+00
(   NA)2(   CO3)     5   1       1.0          -2.6871+02     -2.6972+02    -1.0124+00
( PB+2) (   CO3)     6   1       1.0          -1.7262+02     -1.6723+02     5.3852+00
(   NI) (   CO3)     7   1       1.0          -1.6635+02     -1.6298+02     3.3689+00
(   SR) (   CO3)     8   1       1.0          -2.8670+02     -2.9098+02    -4.2769+00
(   ZN) (   CO3)     9   1       1.0          -1.9826+02     -1.9368+02     4.5868+00

(   AG)2(   SO4)     1   2       1.0          -1.6839+02     -1.7036+02    -1.9669+00
(   BA) (   SO4)     2   2       1.0          -3.5072+02     -3.4999+02     7.3491-01
(   MG) (   SO4)     3   2       1.0          -3.0700+02     -3.0550+02     1.5009+00
( MN+2) (   SO4)     4   2       1.0          -2.4935+02     -2.5395+02    -4.6015+00
(   NA)2(   SO4)     5   2       1.0          -3.3195+02     -3.3064+02     1.3160+00
( PB+2) (   SO4)     6   2       1.0          -2.1914+02     -2.1933+02    -1.9829-01
(   NI) (   SO4)     7   2       1.0          -2.0714+02     -2.1350+02    -6.3639+00
(   SR) (   SO4)     8   2       1.0          -3.4339+02     -3.4497+02    -1.5816+00
(   ZN) (   SO4)     9   2       1.0          -2.4220+02     -2.3369+02     8.5103+00

(   AG)2(   WO4)     1   3       1.0          -2.3573+02     -2.3070+02     5.0295+00
(   BA) (   WO4)     2   3       1.0          -4.0270+02     -4.0613+02    -3.4267+00
(   MG) (   WO4)     3   3       1.0          -3.7365+02     -3.7343+02     2.2050-01
( MN+2) (   WO4)     4   3       1.0          -3.1781+02     -3.1259+02     5.2240+00
(   NA)2(   WO4)     5   3       1.0          -3.8142+02     -3.8260+02    -1.1782+00
( PB+2) (   WO4)     6   3       1.0          -2.8478+02
(   NI) (   WO4)     7   3       1.0          -2.7803+02     -2.7162+02     6.4056+00
(   SR) (   WO4)     8   3       1.0          -3.9934+02     -3.9270+02     6.6380+00
(   ZN) (   WO4)     9   3       1.0          -3.1023+02     -3.2700+02    -1.6768+01

(   AG)2(  MOO4)     1   4       1.0          -2.1155+02     -2.1660+02    -5.0539+00
(   BA) (  MOO4)     2   4       1.0          -3.7657+02
(   MG) ( MOO4)       3   4        1.0           -3.4940+02
( MN+2) ( MOO4)       4   4        1.0           -2.9373+02     -2.8441+02        9.3210+00
(   NA)2( MOO4)       5   4        1.0           -3.5488+02     -3.5405+02        8.3046-01
( PB+2) ( MOO4)       6   4        1.0           -2.6043+02     -2.6565+02       -5.2151+00
(   NI) ( MOO4)       7   4        1.0           -2.5413+02
(   SR) ( MOO4)       8   4        1.0           -3.7380+02
(   ZN) ( MOO4)       9   4        1.0           -2.8611+02


               ROOT MEAN SQUARE ERROR =  5.4213+00    CALORIES/PAIR OF IONIC BONDS
```

```
                              INPUT DATA

              CATIONS =  9          ANIONS =  3          DATA POINTS = 25

                                                       CATIONS PER        CATION
  CATION NO.          CATION          METAL OXIDE      METAL OXIDE        VALENCE
     (I)              CEF(I)                             CIPO(I)          CIV(I)

      1                 CA               CAO            1.000+00             2
      2                 CO               COO            1.000+00             2
      3               FE+2               FEO            1.000+00             2
      4                 LI               LI2O           2.000+00             1
      5                 MG               MGO            1.000+00             2
      6               MN+2               MNO            1.000+00             2
      7                 NA               NA2O           2.000+00             1
      8                 NI               NIO            1.000+00             2
      9                 SR               SRO            1.000+00             2

                                                       ANIONS PER         ANION
  ANION NO.           ANION           ANION ACID        MOLE ACID         VALENCE
     (J)              AEF(J)                             AIPM(J)          AIV(J)

      1                CO3               CO2            1.000+00             2
      2                SO4               SO3            1.000+00             2
      3              AL2O4               AL2O3          1.000+00             2
```

```
                              OUTPUT DATA

      ION                     ION VALUE                EXP VALUE

       CA                      1.2910+01
       CO                      9.1199+00
     FE+2                      8.2391+00
       LI                      1.5689+01
       MG                      9.1527+00
     MN+2                      1.0176+01
       NA                      1.9735+01
       NI                      7.2393+00
       SR                      1.5930+01


      CO3                      0.0000                   1.4439+00
      SO4                     -9.3638+00                1.4529+00
    AL2O4                      5.3052+00                1.3372+00
```

```
                         HEAT OF FORMATION AT 25 DEG C
                              CALORIES/GRAM MOLE

      COMPOUND          I  J    PAIRS OF                     HEAT OF FORMATION
                               IONIC BONDS     CALCULATED         ACTUAL          ERROR

(   CA) (   CO3)        1  1       1.0         -2.8592+02       -2.8811+02     -2.1933+00
(   CO) (   CO3)        2  1       1.0         -1.7541+02       -1.7331+02      2.1027+00
( FE+2) (   CO3)        3  1       1.0         -1.7878+02       -1.7855+02      2.2955-01
(   LI)2(   CO3)        4  1       1.0         -2.8977+02       -2.9026+02     -4.9825-01
(   MG) (   CO3)        5  1       1.0         -2.6209+02       -2.6398+02     -1.8917+00
( MN+2) (   CO3)        6  1       1.0         -2.1444+02       -2.1374+02      6.9461-01
(   NA)2(   CO3)        7  1       1.0         -2.7105+02       -2.6972+02      1.3279+00
(   NI) (   CO3)        8  1       1.0         -1.6871+02       -1.6298+02      5.7276+00
(   SR) (   CO3)        9  1       1.0         -2.8918+02       -2.9098+02     -1.7967+00

(   CA) (   SO4)        1  2       1.0         -3.3697+02       -3.4019+02     -3.2201+00
(   CO) (   SO4)        2  2       1.0         -2.2076+02
( FE+2) (   SO4)        3  2       1.0         -2.2271+02       -2.2041+02      2.2961+00
(   LI)2(   SO4)        4  2       1.0         -3.4468+02       -3.4258+02      2.0927+00
(   MG) (   SO4)        5  2       1.0         -3.0749+02       -3.0550+02      1.9919+00
( MN+2) (   SO4)        6  2       1.0         -2.6144+02
(   NA)2(   SO4)        7  2       1.0         -3.3123+02       -3.3064+02      5.8778-01
(   NI) (   SO4)        8  2       1.0         -2.1095+02       -2.1350+02     -2.5539+00
(   SR) (   SO4)        9  2       1.0         -3.4442+02       -3.4497+02     -5.5356-01

(   CA) (AL2O4)         1  3       1.0         -5.6696+02       -5.5559+02      1.1365+01
(   CO) (AL2O4)         2  3       1.0         -4.6322+02       -4.6653+02     -3.3078+00
( FE+2) (AL2O4)         3  3       1.0         -4.6814+02       -4.7440+02     -6.2623+00
(   LI)2(AL2O4)         4  3       1.0         -5.6552+02       -5.6858+02     -3.0582+00
(   MG) (AL2O4)         5  3       1.0         -5.4984+02       -5.5100+02     -1.1553+00
( MN+2) (AL2O4)         6  3       1.0         -5.0039+02       -5.0109+02     -6.9653-01
(   NA)2(AL2O4)         7  3       1.0         -5.3852+02       -5.4134+02     -2.8167+00
(   NI) (AL2O4)         8  3       1.0         -4.5984+02       -4.6332+02     -3.4822+00
(   SR) (AL2O4)         9  3       1.0         -5.6447+02       -5.5981+02      4.6567+00
```

```
ROOT MEAN SQUARE ERROR =  3.5485+00    CALORIES/PAIR OF IONIC BONDS
```

TABLE II (continued)
COMPUTER INPUT AND OUTPUT DATA

I. DETERMINATION OF ACCURACY OF GROUPING METHOD

B. LARGE GROUP OF ALL ANIONS

```
                                  INPUT DATA

          CATIONS = 16           ANIONS = 10         DATA POINTS = 80

                                                      CATIONS PER        CATION
  CATION NO.          CATION        METAL OXIDE      METAL OXIDE        VALENCE
     (I)              CEF(I)                           CIPO(I)           CIV(I)

      1                 AG             AG2O          2.000+00              1
      2                 BA             BAO           1.000+00              2
      3                 CA             CAO           1.000+00              2
      4                 CD             CDO           1.000+00              2
      5                 CO             COO           1.000+00              2
      6               CU+2             CUO           1.000+00              2
      7               FE+2             FEO           1.000+00              2
      8                  K             K2O           2.000+00              1
      9                 LI             LI2O          2.000+00              1
     10                 MG             MGO           1.000+00              2
     11               MN+2             MNO           1.000+00              2
     12                 NA             NA2O          2.000+00              1
     13                 NI             NIO           1.000+00              2
     14                 PB             PBO           1.000+00              2
     15                 SR             SRO           1.000+00              2
     16                 ZN             ZNO           1.000+00              2


                                                      ANIONS PER         ANION
  ANION NO.           ANION         ANION ACID        MOLE ACID         VALENCE
     (J)              AEF(J)                           AIPM(J)           AIV(J)

      1                CO3             CO2           1.000+00              2
      2                SO4             SO3           1.000+00              2
      3              FE2O4             FE2O3         1.000+00              2
      4               CRO4             CRO3          1.000+00              2
      5               V2O6             V2O5          1.000+00              2
      6                SO3             SO2           1.000+00              2
      7               TIO3             TIO2          1.000+00              2
      8                WO4             WO3           1.000+00              2
      9               MOO4             MOO3          1.000+00              2
     10              AL2O4             AL2O3         1.000+00              2
```

```
                         OUTPUT DATA

     ION                 ION VALUE              EXP VALUE

      AG                  8.7461+00
      BA                  1.7962+01
      CA                  1.2695+01
      CD                  8.3598+00
      CO                  9.3968+00
    CU+2                  3.6575+00
    FE+2                  8.0639+00
       K                  2.3351+01
      LI                  1.5308+01
      MG                  8.5047+00
    MN+2                  8.3561+00
      NA                  1.9764+01
      NI                  6.0760+00
      PB                  9.3167+00
      SR                  1.5502+01
      ZN                  8.0228+00

     CO3                  0.0000                 1.4402+00
     SO4                 -1.0012+01              1.4467+00
   FE2O4                  8.2894+00              1.3906+00
    CRO4                  2.1946-01              1.4403+00
    V2O6                  2.1677+00              1.5063+00
     SO3                 -2.7670+00              1.4403+00
    TIO3                  6.1869+00              1.4000+00
     WO4                 -1.4142+00              1.4274+00
    MOO4                 -1.5668+00              1.4056+00
   AL2O4                  5.6569+00              1.3811+00
```

```
                          HEAT OF FORMATION AT 25 DEG C
                               CALORIES/GRAM MOLE

   COMPOUND          I   J     PAIRS OF                      HEAT OF FORMATION
                              IONIC BONDS      CALCULATED         ACTUAL            ERROR

(   AG)2(   CO3)     1   1        1.0          -1.2403+02      -1.2088+02      3.1461+00
(   BA) (   CO3)     2   1        1.0          -2.9013+02      -2.8716+02      2.9740+00
(   CA) (   CO3)     3   1        1.0          -2.8459+02      -2.8811+02     -3.5249+00
(   CD) (   CO3)     4   1        1.0          -1.7648+02      -1.7846+02     -1.9781+00
(   CO) (   CO3)     5   1        1.0          -1.7628+02      -1.7331+02      2.9659+00
( CU+2) (   CO3)     6   1        1.0          -1.3997+02      -1.4210+02     -2.1253+00
( FE+2) (   CO3)     7   1        1.0          -1.7798+02      -1.7855+02     -5.7027-01
(    K)2(   CO3)     8   1        1.0          -2.7383+02      -2.7187+02      1.9626+00
(   LI)2(   CO3)     9   1        1.0          -2.8739+02      -2.9026+02     -2.8764+00
(   MG) (   CO3)    10   1        1.0          -2.5946+02      -2.6398+02     -4.5264+00
( MN+2) (   CO3)    11   1        1.0          -2.0721+02      -2.1374+02     -6.5308+00
(   NA)2(   CO3)    12   1        1.0          -2.7039+02      -2.6972+02      6.6787-01
(   NI) (   CO3)    13   1        1.0          -1.6472+02      -1.6298+02      1.7413+00
(   PB) (   CO3)    14   1        1.0          -1.7126+02      -1.6723+02      4.0306+00
(   SR) (   CO3)    15   1        1.0          -2.8655+02      -2.9098+02     -4.4290+00
(   ZN) (   CO3)    16   1        1.0          -1.9745+02      -1.9368+02      3.7728+00


(   AG)2(   SO4)     1   2        1.0          -1.7120+02      -1.7036+02      8.4155-01
(   BA) (   SO4)     2   2        1.0          -3.5037+02      -3.4999+02      3.7854-01
(   CA) (   SO4)     3   2        1.0          -3.3775+02      -3.4019+02     -2.4472+00
(   CD) (   SO4)     4   2        1.0          -2.2302+02      -2.2120+02      1.8247+00
(   CO) (   SO4)     5   2        1.0          -2.2449+02
( CU+2) (   SO4)     6   2        1.0          -1.7786+02      -1.8422+02     -6.3509+00
( FE+2) (   SO4)     7   2        1.0          -2.2404+02      -2.2041+02      3.6277+00
(    K)2(   SO4)     8   2        1.0          -3.4062+02      -3.4234+02     -1.7266+00
(   LI)2(   SO4)     9   2        1.0          -3.4416+02      -3.4258+02      1.5762+00
(   MG) (   SO4)    10   2        1.0          -3.0624+02      -3.0550+02      7.3735-01
( MN+2) (   SO4)    11   2        1.0          -2.5375+02      -2.5395+02     -2.0170-01
(   NA)2(   SO4)    12   2        1.0          -3.3288+02      -3.3064+02      2.2384+00
(   NI) (   SO4)    13   2        1.0          -2.0732+02      -2.1350+02     -6.1821+00
(   PB) (   SO4)    14   2        1.0          -2.1935+02      -2.1933+02      1.1709-02
(   SR) (   SO4)    15   2        1.0          -3.4358+02      -3.4497+02     -1.3889+00
(   ZN) (   SO4)    16   2        1.0          -2.4343+02      -2.3369+02      9.7420+00
(   AG)2(FE2O4)      1   3       1.0          -2.0406+02
(   BA)  (FE2O4)     2   3       1.0          -3.5196+02       -3.5049+02       1.4750+00
(   CA)  (FE2O4)     3   3       1.0          -3.5601+02
(   CD)  (FE2O4)     4   3       1.0          -2.5763+02
(   CO)  (FE2O4)     5   3       1.0          -2.5465+02
( CU+2)  (FE2O4)     6   3       1.0          -2.2748+02       -2.3751+02      -1.0026+01
( FE+2)  (FE2O4)     7   3       1.0          -2.6006+02
(    K)2(FE2O4)      8   3       1.0          -3.2623+02
(   LI)2(FE2O4)      9   3       1.0          -3.5395+02       -3.4740+02       6.5500+00
(   MG)  (FE2O4)    10   3       1.0          -3.4017+02       -3.4922+02      -9.0515+00
( MN+2)  (FE2O4)    11   3       1.0          -2.8838+02       -2.9300+02      -4.6245+00
(   NA)2(FE2O4)     12   3       1.0          -3.2906+02
(   NI)  (FE2O4)    13   3       1.0          -2.5067+02       -2.5646+02      -5.7908+00
(   PB)  (FE2O4)    14   3       1.0          -2.4983+02
(   SR)  (FE2O4)    15   3       1.0          -3.5276+02
(   ZN)  (FE2O4)    16   3       1.0          -2.7964+02

(   AG)2( CRO4)      1   4       1.0          -1.7123+02       -1.7237+02      -1.1372+00
(   BA) ( CRO4)      2   4       1.0          -3.3704+02
(   CA) ( CRO4)      3   4       1.0          -3.3165+02       -3.2944+02       2.2049+00
(   CD) ( CRO4)      4   4       1.0          -2.2370+02
(   CO) ( CRO4)      5   4       1.0          -2.2345+02
( CU+2) ( CRO4)      6   4       1.0          -1.8744+02
( FE+2) ( CRO4)      7   4       1.0          -2.2522+02
(    K)2( CRO4)      8   4       1.0          -3.2060+02
(   LI)2( CRO4)      9   4       1.0          -3.3437+02
(   MG) ( CRO4)     10   4       1.0          -3.0667+02
( MN+2) ( CRO4)     11   4       1.0          -2.5443+02
(   NA)2( CRO4)     12   4       1.0          -3.1724+02       -3.1860+02      -1.3553+00
(   NI) ( CRO4)     13   4       1.0          -2.1204+02
(   PB) ( CRO4)     14   4       1.0          -2.1844+02       -2.1750+02       9.4095-01
(   SR) ( CRO4)     15   4       1.0          -3.3352+02
(   ZN) ( CRO4)     16   4       1.0          -2.4468+02

(   AG)2( V2O6)      1   5       1.0          -3.9706+02
(   BA) ( V2O6)      2   5       1.0          -5.6863+02
(   CA) ( V2O6)      3   5       1.0          -5.5908+02       -5.5870+02       3.7746-01
(   CD) ( V2O6)      4   5       1.0          -4.4945+02
(   CO) ( V2O6)      5   5       1.0          -4.4944+02
( CU+2) ( V2O6)      6   5       1.0          -4.1400+02
( FE+2) ( V206)      7    5        1.0          -4.5093+02
(    K)2( V206)      8    5        1.0          -5.5844+02
(   LI)2( V206)      9    5        1.0          -5.6360+02
(   MG) ( V206)     10    5        1.0          -5.3245+02      -5.2790+02       4.5508+00
( MN+2) ( V206)     11    5        1.0          -4.8019+02
(   NA)2( V206)     12    5        1.0          -5.5072+02      -5.5294+02      -2.2184+00
(   NI) ( V206)     13    5        1.0          -4.3774+02
(   PB) ( V206)     14    5        1.0          -4.4441+02
(   SR) ( V206)     15    5        1.0          -5.6291+02
(   ZN) ( V206)     16    5        1.0          -4.7039+02

(   AG)2(  S03)      1    6        1.0          -1.1200+02      -1.1440+02      -2.4034+00
(   BA) (  S03)      2    6        1.0          -2.8177+02      -2.8260+02      -8.3277-01
(   CA) (  S03)      3    6        1.0          -2.7429+02      -2.7588+02      -1.5917+00
(   CD) (  S03)      4    6        1.0          -1.6426+02      -1.6390+02       3.5859-01
(   CO) (  S03)      5    6        1.0          -1.6455+02
( CU+2) (  S03)      6    6        1.0          -1.2499+02
( FE+2) (  S03)      7    6        1.0          -1.6561+02
(    K)2(  S03)      8    6        1.0          -2.6716+02      -2.6690+02       2.6306-01
(   LI)2(  S03)      9    6        1.0          -2.7809+02      -2.7940+02      -1.3097+00
(   MG) (  S03)     10    6        1.0          -2.4731+02      -2.4100+02       6.3077+00
( MN+2) (  S03)     11    6        1.0          -1.9499+02      -1.9737+02      -2.3804+00
(   NA)2(  S03)     12    6        1.0          -2.6261+02      -2.6040+02       2.2139+00
(   NI) (  S03)     13    6        1.0          -1.5128+02
(   PB) (  S03)     14    6        1.0          -1.5950+02      -1.5700+02       2.4992+00
(   SR) (  S03)     15    6        1.0          -2.7733+02      -2.7940+02      -2.0748+00
(   ZN) (  S03)     16    6        1.0          -1.8506+02

(   AG)2( TI03)      1    7        1.0          -2.3653+02
(   BA) ( TI03)      2    7        1.0          -3.8915+02
(   CA) ( TI03)      3    7        1.0          -3.9099+02
(   CD) ( TI03)      4    7        1.0          -2.8964+02
(   CO) ( TI03)      5    7        1.0          -2.8769+02      -2.8946+02      -1.7712+00
( CU+2) ( TI03)      6    7        1.0          -2.6132+02
( FE+2) ( TI03)      7    7        1.0          -2.9167+02
(    K)2( TI03)      8    7        1.0          -3.6537+02
(   LI)2( TI03)      9    7        1.0          -3.9008+02
(   MG) ( TI03)     10    7        1.0          -3.7237+02      -3.7150+02       8.6864-01
( MN+2) ( TI03)     11    7        1.0          -3.2038+02
(   NA)2( TI03)     12    7        1.0          -3.6691+02
(   NI) ( TI03)     13    7        1.0          -2.8272+02      -2.8775+02      -5.0340+00
```

```
   (   PB) ( TIO3)     14   7      1.0        -2.8280+02
   (   SR) ( TIO3)     15   7      1.0        -3.8898+02
   (   ZN) ( TIO3)     16   7      1.0        -3.1121+02    -3.0927+02     1.9448+00

   (   AG)2(  WO4)      1   8      1.0        -2.3613+02    -2.3070+02     5.4320+00
   (   BA) (  WO4)      2   8      1.0        -4.0232+02    -4.0613+02    -3.8116+00
   (   CA) (  WO4)      3   8      1.0        -3.9692+02
   (   CD) (  WO4)      4   8      1.0        -2.8854+02
   (   CO) (  WO4)      5   8      1.0        -2.8844+02
   ( CU+2) (  WO4)      6   8      1.0        -2.5110+02
   ( FE+2) (  WO4)      7   8      1.0        -2.9001+02
   (    K)2(  WO4)      8   8      1.0        -3.8546+02
   (   LI)2(  WO4)      9   8      1.0        -3.9970+02
   (   MG) (  WO4)     10   8      1.0        -3.7153+02    -3.7343+02    -1.8954+00
   ( MN+2) (  WO4)     11   8      1.0        -3.1927+02    -3.1259+02     6.6828+00
   (   NA)2(  WO4)     12   8      1.0        -3.8243+02    -3.8260+02    -1.7236-01
   (   NI) (  WO4)     13   8      1.0        -2.7644+02    -2.7162+02     4.8170+00
   (   PB) (  WO4)     14   8      1.0        -2.8342+02
   (   SR) (  WO4)     15   8      1.0        -3.9886+02    -3.9270+02     6.1610+00
 X (   ZN) (  WO4)     16   8      1.0        -3.0947+02    -3.2700+02    -1.7531+01

   (   AG)2( MOO4)      1   9      1.0        -2.1176+02    -2.1660+02    -4.8433+00
   (   BA) ( MOO4)      2   9      1.0        -3.7515+02
   (   CA) ( MOO4)      3   9      1.0        -3.7152+02
   (   CD) ( MOO4)      4   9      1.0        -2.6425+02
   (   CO) ( MOO4)      5   9      1.0        -2.6392+02
   ( CU+2) ( MOO4)      6   9      1.0        -2.2759+02
   ( FE+2) ( MOO4)      7   9      1.0        -2.6578+02
   (    K)2( MOO4)      8   9      1.0        -3.5607+02
   (   LI)2( MOO4)      9   9      1.0        -3.7348+02
   (   MG) ( MOO4)     10   9      1.0        -3.4721+02
  *( MN+2) ( MOO4)     11   9      1.0        -2.9498+02    -2.8441+02     1.0573+01
   (   NA)2( MOO4)     12   9      1.0        -3.5456+02    -3.5405+02     5.0682-01
   (   NI) ( MOO4)     13   9      1.0        -2.5259+02
   (   PB) ( MOO4)     14   9      1.0        -2.5891+02    -2.6565+02    -6.7379+00
   (   SR) ( MOO4)     15   9      1.0        -3.7257+02
   (   ZN) ( MOO4)     16   9      1.0        -2.8525+02

   (   AG)2(AL2O4)      1  10      1.0        -4.1221+02
   (   BA) (AL2O4)      2  10      1.0        -5.6426+02
```

```
* (   CA) (AL204)     3  10       1.0         -5.6669+02      -5.5559+02      1.1098+01
  (   CD) (AL204)     4  10       1.0         -4.6529+02
  (   CO) (AL204)     5  10       1.0         -4.6341+02      -4.6653+02     -3.1164+00
  ( CU+2) (AL204)     6  10       1.0         -4.3704+02
  ( FE+2) (AL204)     7  10       1.0         -4.6728+02      -4.7440+02     -7.1160+00
  (    K)2(AL204)     8  10       1.0         -5.3941+02
  (   LI)2(AL204)     9  10       1.0         -5.6556+02      -5.6858+02     -3.0215+00
  (   MG) (AL204)    10  10       1.0         -5.4803+02      -5.5100+02     -2.9722+00
  ( MN+2) (AL204)    11  10       1.0         -4.9603+02      -5.0109+02     -5.0629+00
  (   NA)2(AL204)    12  10       1.0         -5.4171+02      -5.4134+02      3.7054-01
  (   NI) (AL204)    13  10       1.0         -4.5772+02      -4.6332+02     -5.5973+00
  (   PB) (AL204)    14  10       1.0         -4.5852+02
  (   SR) (AL204)    15  10       1.0         -5.6443+02      -5.5981+02      4.6193+00
  (   ZN) (AL204)    16  10       1.0         -4.8682+02


          ROOT MEAN SQUARE ERROR =  4.6515+00    CALORIES/PAIR OF IONIC BONDS
```

TABLE II (continued)
COMPUTER INPUT AND OUTPUT DATA

II. ESTIMATION OF UNKNOWN HEATS

TABLE II

VALUES OF K_i, A_j, and N_j FOR ESTIMATING HEAT OF FORMATION USING THE ERDÖS METHOD

ION	ION VALUE	EXP VALUE
AG	8.9734+00	
BA	1.8179+01	
CA	1.3095+01	
CD	8.5344+00	
CO	8.9525+00	
CU+2	4.5279+00	
FE+2	8.2522+00	
K	2.3728+01	
LI	1.5391+01	
MG	8.6846+00	
MN+2	9.0979+00	
NA	1.9968+01	
NI	7.4604+00	
PB	9.3412+00	
SR	1.5738+01	
ZN	6.5586+00	
AL+3	4.3695+00	
BE	4.9321+00	
BI+3	7.7466+00	
CE+4	9.0542+00	
CS	2.5307+01	
CU+1	4.0770+00	
FE+3	4.2917+00	
MN+3	5.4745+00	
RB	2.4595+01	
SB+3	3.2368+00	
SN+4	1.4090+00	
TH+4	7.7294+00	
U+4	6.7985+00	
ZR+4	9.8665+00	
CO3	0.0000	1.4335+00
SO4	-9.7717+00	1.4451+00

TABLE II (continued)

FE2O4	7.4455+00	1.3895+00
CRO4	1.3474-01	1.4282+00
V2O6	1.5543+00	1.4716+00
SO3	-2.6035+00	1.4379+00
TIO3	5.1345+00	1.4000+00
WO4	8.7467-01	1.4812+00
MOO4	-2.8685+00	1.3804+00
AL2O4	5.2373+00	1.3823+00
CR2O4	1.2341+00	1.6719+00

TABLE I

HEAT OF FORMATION AT 25 DEG C
(KCAL/GMOLE)

COMPOUND	I	J	PAIRS OF IONIC BONDS	CALCULATED	HEAT OF FORMATION ACTUAL	ERROR
(AG)2(CO3)	1	1	1.0	-1.2454+02	-1.2088+02	3.6599+00
(BA) (CO3)	2	1	1.0	-2.9000+02	-2.8716+02	2.8460+00
(CA) (CO3)	3	1	1.0	-2.8568+02	-2.8811+02	-2.4366+00
(CD) (CO3)	4	1	1.0	-1.7681+02	-1.7846+02	-1.6454+00
(CO) (CO3)	5	1	1.0	-1.7424+02	-1.7331+02	9.2835-01
(CU+2) (CO3)	6	1	1.0	-1.4221+02	-1.4210+02	1.1684-01
(FE+2) (CO3)	7	1	1.0	-1.7838+02	-1.7855+02	-1.7829-01
(K)2(CO3)	8	1	1.0	-2.7402+02	-2.7187+02	2.1538+00
(LI)2(CO3)	9	1	1.0	-2.8687+02	-2.9026+02	-3.3984+00
(MG) (CO3)	10	1	1.0	-2.5980+02	-2.6398+02	-4.1796+00
(MN+2) (CO3)	11	1	1.0	-2.0963+02	-2.1374+02	-4.1091+00
(NA)2(CO3)	12	1	1.0	-2.7001+02	-2.6972+02	2.8867-01
(NI) (CO3)	13	1	1.0	-1.6910+02	-1.6298+02	6.1260+00
(PB) (CO3)	14	1	1.0	-1.7099+02	-1.6723+02	3.7567+00
(SR) (CO3)	15	1	1.0	-2.8673+02	-2.9098+02	-4.2510+00
(ZN) (CO3)	16	1	1.0	-1.9221+02	-1.9368+02	-1.4677+00
(AL+3)2(CO3)3	17	1	3.0	-7.0703+02		
(BE) (CO3)	18	1	1.0	-2.4689+02		
(BI+3)2(CO3)3	19	1	3.0	-4.7657+02		
(CE+4) (CO3)2	20	1	2.0	-4.6801+02		
(CS)2(CO3)	21	1	1.0	-2.7257+02	-2.7447+02	-1.9008+00
(CU+1)2(CO3)	22	1	1.0	-1.4229+02		
(FE+3)2(CO3)3	23	1	3.0	-5.0266+02		
(MN+3)2(CO3)3	24	1	3.0	-5.4546+02		
(RB)2(CO3)	25	1	1.0	-2.7144+02	-2.6948+02	1.9589+00
(SB+3)2(CO3)3	26	1	3.0	-4.6809+02		
(SN+4) (CO3)2	27	1	2.0	-3.3004+02		
(TH+4) (CO3)2	28	1	2.0	-5.1962+02		
(U+4) (CO3)2	29	1	2.0	-4.7820+02		
(ZR+4) (CO3)2	30	1	2.0	-5.0261+02		
(AG)2(SO4)	1	2	1.0	-1.7082+02	-1.7036+02	4.5900-01
(BA) (SO4)	2	2	1.0	-3.4958+02	-3.4999+02	-4.0657-01
(CA) (SO4)	3	2	1.0	-3.3624+02	-3.4019+02	-1.9570+00

TABLE I (continued)

(CD) (SO4)	4	2	1.0	-2.2237+02	-2.2120+02	1.1760+00
(CO) (SO4)	5	2	1.0	-2.2048+02		
(CU+2) (SO4)	6	2	1.0	-1.8064+02	-1.8422+02	-3.5806+00
(FE+2) (SO4)	7	2	1.0	-2.2347+02	-2.2041+02	3.0621+00
(K)2(SO4)	8	2	1.0	-3.4070+02	-3.4234+02	-1.6451+00
(LI)2(SO4)	9	2	1.0	-3.4267+02	-3.4258+02	9.0534-02
(MG) (SO4)	10	2	1.0	-3.0561+02	-3.0550+02	1.1123-01
(MN+2) (SO4)	11	2	1.0	-2.5611+02	-2.5395+02	2.1601+00
(NA)2(SO4)	12	2	1.0	-3.3192+02	-3.3064+02	1.2868+00
(NI) (SO4)	13	2	1.0	-2.1287+02	-2.1350+02	-6.3629-01
(PB) (SO4)	14	2	1.0	-2.1785+02	-2.1933+02	-1.4813+00
(SR) (SO4)	15	2	1.0	-3.4302+02	-3.4497+02	-1.9566+00
(ZN) (SO4)	16	2	1.0	-2.3441+02	-2.3369+02	7.1504-01
(AL+3)2(SO4)3	17	2	3.0	-8.2135+02	-8.2038+02	9.7059-01
(BE) (SO4)	18	2	1.0	-2.8610+02	-2.8565+02	4.4514-01
(BI+3)2(SO4)3	19	2	3.0	-6.0932+02	-6.0810+02	1.2200+00
(CE+4) (SO4)2	20	2	2.0	-5.6083+02	-5.6000+02	8.2569-01
(CS)2(SO4)	21	2	1.0	-3.4119+02	-3.3900+02	2.1918+00
(CU+1)2(SO4)	22	2	1.0	-1.7981+02	-1.7951+02	3.0120-01
(FE+3)2(SO4)3	23	2	3.0	-6.1652+02	-6.1560+02	9.2418-01
(MN+3)2(SO4)3	24	2	3.0	-6.6615+02	-6.6690+02	-7.5377-01
(RB)2(SO4)	25	2	1.0	-3.3919+02	-3.4019+02	-1.0078+00
(SB+3)2(SO4)3	26	2	3.0	-5.7542+02	-5.7420+02	1.2166+00
(SN+4) (SO4)2	27	2	2.0	-3.9308+02	-3.9340+02	-3.2331-01
(TH+4) (SO4)2	28	2	2.0	-6.0807+02	-6.0726+02	8.0502-01
(U+4) (SO4)2	29	2	2.0	-5.6344+02	-5.6300+02	4.4153-01
(ZR+4) (SO4)2	30	2	2.0	-5.9801+02	-5.9701+02	9.9767-01
(AG)2(FE2O4)	1	3	1.0	-2.0553+02		
(BA) (FE2O4)	2	3	1.0	-3.5555+02	-3.5049+02	5.0564+00
(CA) (FE2O4)	3	3	1.0	-3.5924+02		
(CD) (FE2O4)	4	3	1.0	-2.5873+02		
(CO) (FE2O4)	5	3	1.0	-2.5526+02		
(CU+2) (FE2O4)	6	3	1.0	-2.3149+02	-2.3751+02	-6.0234+00
(FE+2) (FE2O4)	7	3	1.0	-2.6093+02		
(K)2(FE2O4)	8	3	1.0	-3.3105+02		
(LI)2(FE2O4)	9	3	1.0	-3.5674+02	-3.4740+02	9.3391+00
(MG) (FE2O4)	10	3	1.0	-3.4140+02	-3.4922+02	-7.8227+00
(MN+2) (FE2O4)	11	3	1.0	-2.9036+02	-2.9300+02	-2.6383+00
(NA)2(FE2O4)	12	3	1.0	-3.3280+02		
(NI) (FE2O4)	13	3	1.0	-2.5367+02	-2.5646+02	-2.7692+00
(PB) (FE2O4)	14	3	1.0	-2.5122+02		

TABLE I (continued)

(SR) (FE204)	15	3	1.0	-3.5606+02		
(ZN) (FE204)	16	3	1.0	-2.7895+02		
(AL+3)2(FE204)3	17	3	3.0	-9.7513+02		
(BE) (FE204)	18	3	1.0	-3.3585+02		
(BI+3)2(FE204)3	19	3	3.0	-7.2792+02		
(CE+4) (FE204)2	20	3	2.0	-6.2965+02		
(CS)2(FE204)	21	3	1.0	-3.2716+02		
(CU+1)2(FE204)	22	3	1.0	-2.3180+02		
(FE+3)2(FE204)3	23	3	3.0	-7.7090+02		
(MN+3)2(FE204)3	24	3	3.0	-8.1067+02		
(RB)2(FE204)	25	3	1.0	-3.2713+02		
(SB+3)2(FE204)3	26	3	3.0	-7.3707+02		
(SN+4) (FE204)2	27	3	2.0	-5.0728+02		
(TH+4) (FE204)2	28	3	2.0	-6.8728+02		
(U+4) (FE204)2	29	3	2.0	-6.5072+02		
(ZR+4) (FE204)2	30	3	2.0	-6.6104+02		

(AG)2(CR04)	1	4	1.0	-1.7180+02	-1.7237+02	-5.7195-01
(BA) (CR04)	2	4	1.0	-3.3637+02		
(CA) (CR04)	3	4	1.0	-3.3257+02	-3.2944+02	3.1271+00
(CD) (CR04)	4	4	1.0	-2.2410+02		
(CO) (CR04)	5	4	1.0	-2.2149+02		
(CU+2) (CR04)	6	4	1.0	-1.8980+02		
(FE+2) (CR04)	7	4	1.0	-2.2569+02		
(K)2(CR04)	8	4	1.0	-3.1972+02		
(LI)2(CR04)	9	4	1.0	-3.3353+02		
(MG) (CR04)	10	4	1.0	-3.0708+02		
(MN+2) (CR04)	11	4	1.0	-2.5688+02		
(NA)2(CR04)	12	4	1.0	-3.1617+02	-3.1860+02	-2.4304+00
(NI) (CR04)	13	4	1.0	-2.1648+02		
(PB) (CR04)	14	4	1.0	-2.1821+02	-2.1750+02	7.1153-01
(SR) (CR04)	15	4	1.0	-3.3336+02		
(ZN) (CR04)	16	4	1.0	-2.3965+02		
(AL+3)2(CR04)3	17	4	3.0	-8.4981+02		
(BE) (CR04)	18	4	1.0	-2.9444+02		
(BI+3)2(CR04)3	19	4	3.0	-6.1862+02		
(CE+4) (CR04)2	20	4	2.0	-5.6251+02		
(CS)2(CR04)	21	4	1.0	-3.1806+02		
(CU+1)2(CR04)	22	4	1.0	-1.8990+02		
(FE+3)2(CR04)3	23	4	3.0	-6.4546+02		
(MN+3)2(CR04)3	24	4	3.0	-6.8801+02		
(RB)2(CR04)	25	4	1.0	-3.1702+02		

TABLE I (continued)

(SB+3)2(CRO4)3	26	4	3.0	-6.1109+02		
(SN+4) (CRO4)2	27	4	2.0	-4.2563+02		
(TH+4) (CRO4)2	28	4	2.0	-6.1433+02		
(U+4) (CRO4)2	29	4	2.0	-5.7304+02		
(ZR+4) (CRO4)2	30	4	2.0	-5.9697+02		
(AG)2(V2O6)	1	5	1.0	-3.9907+02		
(BA) (V2O6)	2	5	1.0	-5.6734+02		
(CA) (V2O6)	3	5	1.0	-5.6098+02	-5.5870+02	2.2825+00
(CD) (V2O6)	4	5	1.0	-4.5132+02		
(CO) (V2O6)	5	5	1.0	-4.4877+02		
(CU+2) (V2O6)	6	5	1.0	-4.1715+02		
(FE+2) (V2O6)	7	5	1.0	-4.5287+02		
(K)2(V2O6)	8	5	1.0	-5.5466+02		
(LI)2(V2O6)	9	5	1.0	-5.6295+02		
(MG) (V2O6)	10	5	1.0	-5.3432+02	-5.2790+02	6.4164+00
(MN+2) (V2O6)	11	5	1.0	-4.8418+02		
(NA)2(V2O6)	12	5	1.0	-5.4829+02	-5.5294+02	-4.6518+00
(NI) (V2O6)	13	5	1.0	-4.4359+02		
(PB) (V2O6)	14	5	1.0	-4.4555+02		
(SR) (V2O6)	15	5	1.0	-5.6296+02		
(ZN) (V2O6)	16	5	1.0	-4.6675+02		
(AL+3)2(V2O6)3	17	5	3.0	-1.5320+03		
(BE) (V2O6)	18	5	1.0	-5.2171+02		
(BI+3)2(V2O6)3	19	5	3.0	-1.3000+03		
(CE+4) (V2O6)2	20	5	2.0	-1.0171+03		
(CS)2(V2O6)	21	5	1.0	-5.5433+02		
(CU+1)2(V2O6)	22	5	1.0	-4.1737+02		
(FE+3)2(V2O6)3	23	5	3.0	-1.3277+03		
(MN+3)2(V2O6)3	24	5	3.0	-1.3696+03		
(RB)2(V2O6)	25	5	1.0	-5.5268+02		
(SB+3)2(V2O6)3	26	5	3.0	-1.2944+03		
(SN+4) (V2O6)2	27	5	2.0	-8.8400+02		
(TH+4) (V2O6)2	28	5	2.0	-1.0686+03		
(U+4) (V2O6)2	29	5	2.0	-1.0272+03		
(ZR+4) (V2O6)2	30	5	2.0	-1.0519+03		
(AG)2(SO3)	1	6	1.0	-1.1207+02	-1.1440+02	-2.3340+00
(BA) (SO3)	2	6	1.0	-2.8148+02	-2.8260+02	-1.1171+00
(CA) (SO3)	3	6	1.0	-2.7508+02	-2.7588+02	-7.9761-01
(CD) (SO3)	4	6	1.0	-1.6412+02	-1.6390+02	2.1793-01

TABLE I (continued)

(CO) (SO3)	5	6	1.0	-1.6175+02		
(CU+2) (SO3)	6	6	1.0	-1.2728+02		
(FE+2) (SO3)	7	6	1.0	-1.4554+02		
(K)2(SO3)	8	6	1.0	-2.6759+02	-2.6690+02	6.8863-01
(LI)2(SO3)	9	6	1.0	-2.7723+02	-2.7940+02	-2.1664+00
(MG) (SO3)	10	6	1.0	-2.4718+02	-2.4100+02	6.1849+00
(MN+2) (SO3)	11	6	1.0	-1.9722+02	-1.9737+02	-1.5163-01
(NA)2(SO3)	12	6	1.0	-2.6217+02	-2.6040+02	1.7728+00
(NI) (SO3)	13	6	1.0	-1.5586+02		
(PB) (SO3)	14	6	1.0	-1.5869+02	-1.5700+02	1.6886+00
(SR) (SO3)	15	6	1.0	-2.7724+02	-2.7940+02	-2.1613+00
(ZN) (SO3)	16	6	1.0	-1.7848+02		
(AL+3)2(SO3)3	17	6	3.0	-6.6191+02		
(BE) (SO3)	18	6	1.0	-2.3221+02		
(BI+3)2(SO3)3	19	6	3.0	-4.3728+02		
(CE+4) (SO3)2	20	6	2.0	-4.4314+02		
(CS)2(SO3)	21	6	1.0	-2.6471+02		
(CU+1)2(SO3)	22	6	1.0	-1.2706+02		
(FE+3)2(SO3)3	23	6	3.0	-4.5740+02		
(MN+3)2(SO3)3	24	6	3.0	-5.0239+02		
(RB)2(SO3)	25	6	1.0	-2.6532+02		
(SB+3)2(SO3)3	26	6	3.0	-4.2064+02		
(SN+4) (SO3)2	27	6	2.0	-2.9536+02		
(TH+4) (SO3)2	28	6	2.0	-4.9341+02		
(U+4) (SO3)2	29	6	2.0	-4.5100+02		
(ZR+4) (SO3)2	30	6	2.0	-4.7852+02		
(AG)2(TIO3)	1	7	1.0	-2.3937+02		
(BA) (TIO3)	2	7	1.0	-3.9401+02		
(CA) (TIO3)	3	7	1.0	-3.9548+02		
(CD) (TIO3)	4	7	1.0	-2.9223+02		
(CO) (TIO3)	5	7	1.0	-2.8910+02	-2.8946+02	-3.6440-01
(CU+2) (TIO3)	6	7	1.0	-2.6449+02		
(FE+2) (TIO3)	7	7	1.0	-2.9417+02		
(K)2(TIO3)	8	7	1.0	-3.7172+02		
(LI)2(TIO3)	9	7	1.0	-3.9403+02		
(MG) (TIO3)	10	7	1.0	-3.7502+02	-3.7150+02	3.5172+00
(MN+2) (TIO3)	11	7	1.0	-3.2430+02		
(NA)2(TIO3)	12	7	1.0	-3.7199+02		
(NI) (TIO3)	13	7	1.0	-2.8602+02	-2.8775+02	-1.7280+00
(PB) (TIO3)	14	7	1.0	-2.8534+02		
(SR) (TIO3)	15	7	1.0	-3.9350+02		

TABLE I (continued)

(ZN) (TIO3)	16	7	1.0	-3.1051+02	-3.0927+02	1.2441+00
(AL+3)2(TIO3)3	17	7	3.0	-1.0746+03		
(BE) (TIO3)	18	7	1.0	-3.6842+02		
(BI+3)2(TIO3)3	19	7	3.0	-8.2608+02		
(CE+4) (TIO3)2	20	7	2.0	-6.9746+02		
(CS)2(TIO3)	21	7	1.0	-3.6844+02		
(CU+1)2(TIO3)	22	7	1.0	-2.6520+02		
(FE+3)2(TIO3)3	23	7	3.0	-8.7056+02		
(MN+3)2(TIO3)3	24	7	3.0	-9.0626+02		
(RB)2(TIO3)	25	7	1.0	-3.6813+02		
(SB+3)2(TIO3)3	26	7	3.0	-8.3904+02		
(SN+4) (TIO3)2	27	7	2.0	-5.7714+02		
(TH+4) (TIO3)2	28	7	2.0	-7.5268+02		
(U+4) (TIO3)2	29	7	2.0	-7.1404+02		
(ZR+4) (TIO3)2	30	7	2.0	-7.2998+02		
(AG)2(WO4)	1	8	1.0	-2.3092+02	-2.3070+02	2.2073-01
(BA) (WO4)	2	8	1.0	-4.0176+02	-4.0613+02	-4.3662+00
(CA) (WO4)	3	8	1.0	-3.9394+02		
(CD) (WO4)	4	8	1.0	-2.8305+02		
(CO) (WO4)	5	8	1.0	-2.8061+02		
(CU+2) (WO4)	6	8	1.0	-2.4776+02		
(FE+2) (WO4)	7	8	1.0	-2.8452+02		
(K)2(WO4)	8	8	1.0	-3.9084+02		
(LI)2(WO4)	9	8	1.0	-3.9656+02		
(MG) (WO4)	10	8	1.0	-3.6609+02	-3.7343+02	-7.3437+00
(MN+2) (WO4)	11	8	1.0	-3.1606+02	-3.1259+02	3.4651+00
(NA)2(WO4)	12	8	1.0	-3.8326+02	-3.8260+02	6.6410-01
(NI) (WO4)	13	8	1.0	-2.7504+02	-2.7162+02	3.4174+00
(PB) (WO4)	14	8	1.0	-2.7749+02		
(SR) (WO4)	15	8	1.0	-3.9667+02	-3.9270+02	3.9654+00
(ZN) (WO4)	16	8	1.0	-2.9795+02		
(AL+3)2(WO4)3	17	8	3.0	-1.0237+03		
(BE) (WO4)	18	8	1.0	-3.5245+02		
(BI+3)2(WO4)3	19	8	3.0	-7.9459+02		
(CE+4) (WO4)2	20	8	2.0	-6.8082+02		
(CS)2(WO4)	21	8	1.0	-3.9104+02		
(CU+1)2(WO4)	22	8	1.0	-2.4785+02		
(FE+3)2(WO4)3	23	8	3.0	-8.1932+02		
(MN+3)2(WO4)3	24	8	3.0	-8.6224+02		
(RB)2(WO4)	25	8	1.0	-3.8916+02		
(SB+3)2(WO4)3	26	8	3.0	-7.8500+02		

TABLE I (continued)

```
( SN+4) (  WO4)2    27   8     2.0        -5.4246+02
( TH+4) (  WO4)2    28   8     2.0        -7.3163+02
(  U+4) (  WO4)2    29   8     2.0        -6.8978+02
( ZR+4) (  WO4)2    30   8     2.0        -7.1602+02

(    AG)2( MOO4)     1   9     1.0        -2.1551+02     -2.1660+02     -1.0907+00
(    BA) ( MOO4)     2   9     1.0        -3.7704+02
(    CA) ( MOO4)     3   9     1.0        -3.7541+02
(    CD) ( MOO4)     4   9     1.0        -2.6785+02
(    CO) ( MOO4)     5   9     1.0        -2.6521+02
( CU+2) ( MOO4)     6   9     1.0        -2.3321+02
( FE+2) ( MOO4)     7   9     1.0        -2.6945+02
(     K)2( MOO4)     8   9     1.0        -3.5690+02
(    LI)2( MOO4)     9   9     1.0        -3.7552+02
(    MG) ( MOO4)    10   9     1.0        -3.5082+02
( MN+2) ( MOO4)    11   9     1.0        -3.0058+02
(    NA)2( MOO4)    12   9     1.0        -3.5583+02     -3.5405+02      1.7776+00
(    NI) ( MOO4)    13   9     1.0        -2.6026+02
(    PB) ( MOO4)    14   9     1.0        -2.6188+02     -2.6565+02     -3.7668+00
(    SR) ( MOO4)    15   9     1.0        -3.7520+02
(    ZN) ( MOO4)    16   9     1.0        -2.8339+02
( AL+3)2( MOO4)3    17   9     3.0        -9.7992+02
(    BE) ( MOO4)    18   9     1.0        -3.3796+02
( BI+3)2( MOO4)3    19   9     3.0        -7.4996+02
( CE+4) ( MOO4)2    20   9     2.0        -6.4992+02
(    CS)2( MOO4)    21   9     1.0        -3.5407+02
( CU+1)2( MOO4)    22   9     1.0        -2.3318+02
( FE+3)2( MOO4)3    23   9     3.0        -7.7550+02
( MN+3)2( MOO4)3    24   9     3.0        -8.1886+02
(    RB)2( MOO4)    25   9     1.0        -3.5357+02
( SB+3)2( MOO4)3    26   9     3.0        -7.4001+02
( SN+4) ( MOO4)2    27   9     2.0        -5.0939+02
( TH+4) ( MOO4)2    28   9     2.0        -7.0189+02
(  U+4) ( MOO4)2    29   9     2.0        -6.6057+02
( ZR+4) ( MOO4)2    30   9     2.0        -6.8418+02

(    AG)2(AL2O4)     1  10     1.0        -4.1364+02
(    BA) (AL2O4)     2  10     1.0        -5.6667+02
(    CA) (AL2O4)     3  10     1.0        -5.6916+02
(    CD) (AL2O4)     4  10     1.0        -4.6654+02
(    CO) (AL2O4)     5  10     1.0        -4.6337+02     -4.6653+02     -3.1633+00
```

RB,

TABLE I (continued)

(CU+2) (AL2O4)	6	10	1.0	-4.3703+02		
(FE+2) (AL2O4)	7	10	1.0	-4.6852+02	-4.7440+02	-5.8829+00
(K)2(AL2O4)	8	10	1.0	-5.4292+02		
(LI)2(AL2O4)	9	10	1.0	-5.6729+02	-5.6853+02	-1.2882+00
(MG) (AL2O4)	10	10	1.0	-5.4932+02	-5.5100+02	-1.6829+00
(MN+2) (AL2O4)	11	10	1.0	-4.9856+02	-5.0109+02	-2.5334+00
(NA)2(AL2O4)	12	10	1.0	-5.4422+02	-5.4134+02	2.8800+00
(NI) (AL2O4)	13	10	1.0	-4.6044+02	-4.6332+02	-2.8810+00
(PB) (AL2O4)	14	10	1.0	-4.5957+02		
(SR) (AL2O4)	15	10	1.0	-5.6669+02	-5.5981+02	6.8826+00
(ZN) (AL2O4)	16	10	1.0	-4.8500+02		
(AL+3)2(AL2O4)3	17	10	3.0	-1.5982+03		
(BE) (AL2O4)	18	10	1.0	-5.4299+02		
(BI+3)2(AL2O4)3	19	10	3.0	-1.3493+03		
(CE+4) (AL2O4)2	20	10	2.0	-1.0460+03		
(CS)2(AL2O4)	21	10	1.0	-5.3918+02		
(CU+1)2(AL2O4)	22	10	1.0	-4.3971+02		
(FE+3)2(AL2O4)3	23	10	3.0	-1.3941+03		
(MN+3)2(AL2O4)3	24	10	3.0	-1.4300+03		
(RB)2(AL2O4)	25	10	1.0	-5.3909+02		
(SB+3)2(AL2O4)3	26	10	3.0	-1.3625+03		
(SN+4) (AL2O4)2	27	10	2.0	-9.2628+02		
(TH+4) (AL2O4)2	28	10	2.0	-1.1015+03		
(U+4) (AL2O4)2	29	10	2.0	-1.0630+03		
(ZR+4) (AL2O4)2	30	10	2.0	-1.0783+03		
(AG)2(CR2O4)	1	3	1.0	-3.0820+02		
(BA) (CR2O4)	2	3	1.0	-5.1632+02		
(CA) (CR2O4)	3	3	1.0	-4.9165+02	-4.9240+02	-7.4862-01
(CD) (CR2O4)	4	3	1.0	-3.6166+02		
(CO) (CR2O4)	5	3	1.0	-3.5232+02	-3.5064+02	1.6814+00
(CU+2) (CR2O4)	6	3	1.0	-3.2174+02		
(FE+2) (CR2O4)	7	3	1.0	-3.6022+02		
(K)2(CR2O4)	8	3	1.0	-5.4119+02		
(LI)2(CR2O4)	9	3	1.0	-5.0189+02		
(MG) (CR2O4)	10	3	1.0	-4.4739+02		
(MN+2) (CR2O4)	11	3	1.0	-3.9672+02		
(NA)2(CR2O4)	12	3	1.0	-5.0814+02		
(NI) (CR2O4)	13	3	1.0	-3.4874+02		
(PB) (CR2O4)	14	3	1.0	-3.5723+02		

TABLE I (continued)

```
(    SR) (CR204)      15    3        1.0           -5.1463+02
(    ZN) (CR204)      16    3        1.0           -3.7283+02
( AL+3)2(CR204)3      17    3        3.0           -1.2380+03
(    BE) (CR204)      18    3        1.0           -4.2443+02
( BI+3)2(CR204)3      19    3        3.0           -1.0240+03
( CE+4) (CR204)2      20    3        2.0           -8.3979+02
(    CS)2(CR204)      21    3        1.0           -5.5192+02
( CU+1)2(CR204)       22    3        1.0           -3.1904+02
( FE+3)2(CR204)3      23    3        3.0           -1.0334+03
( MN+3)2(CR204)3      24    3        3.0           -1.0802+03
(    RB)2(CR204)      25    3        1.0           -5.4497+02
( SB+3)2(CR204)3      26    3        3.0           -9.9712+02
( SN+4) (CR204)2      27    3        2.0           -6.8403+02
( TH+4) (CR204)2      28    3        2.0           -8.8449+02
(  U+4) (CR204)2      29    3        2.0           -8.3908+02
( ZR+4) (CR204)2      30    3        2.0           -8.7929+02



ROOT MEAN SQUARE ERROR =  3.0250+00    CALORIES/PAIR OF IONIC BONDS
```

more than 10 kilocalories different from the value predicted by our correlation, we did not use the data as a basis for predicting other heats of formation by our method. The value was still included in the TRACOR data base with the appropriate reference. For example, the heats of formation of $ZnWO_4$ and $CaAl_2O_4$ showed errors of 17.5 and 11.1 kilocalories respectively. These values are found in the TRACOR data base, but they were not used to predict the heats of formation of other aluminates or wolframates.

The accepted values for heats of formation that were used in the correlation and estimation were obtained from the TRACOR data base. Table III gives all of the data used in the estimation of unknown heats of formation. The "Heat of Reaction" in Table III refers to the reaction between a "base" or metal oxide such as BaO, and an "acid," such as CO_2, SO_3, or Al_2O_3, to yield a product compound, such as $BaCO_3$, $BaSO_4$, or $BaAl_2O_4$. The heats of formation of the oxides, acids, and product compounds are found in the three columns on the right in Table III.

I. Parsons

TABLE III

HEATS OF FORMATION FROM THE TRACOR DATA BASE USED IN ESTIMATING UNKNOWN HEATS OF FORMATION

```
   COMPOUND          MOLES         MOLES     HEAT OF REACTION     HEATS OF FORMATION KCAL/GMOLE
                     OXIDE         ACID       KCAL/GMOLE        OXIDE           ACID         COMPOUND


 AG2CO3            1.0000+00     1.0000+00    -1.9573+01     -7.3008+00     -9.4010+01     -1.2088+02
 BACO3             1.0000+00     1.0000+00    -6.1075+01     -1.3207+02     -9.4010+01     -2.8716+02
 CACO3             1.0000+00     1.0000+00    -4.2378+01     -1.5173+02     -9.4010+01     -2.8811+02
 CDCO3             1.0000+00     1.0000+00    -2.3266+01     -6.1182+01     -9.4010+01     -1.7846+02
 COCO3             1.0000+00     1.0000+00    -2.2227+01     -5.7073+01     -9.4010+01     -1.7331+02
 CUCO3             1.0000+00     1.0000+00    -8.5980+00     -3.9490+01     -9.4010+01     -1.4210+02
 FECO3             1.0000+00     1.0000+00    -2.0782+01     -6.3762+01     -9.4010+01     -1.7855+02
 K2CO3             1.0000+00     1.0000+00    -9.1496+01     -8.6362+01     -9.4010+01     -2.7187+02
 LI2CO3            1.0000+00     1.0000+00    -5.3750+01     -1.4250+02     -9.4010+01     -2.9026+02
 MGCO3             1.0000+00     1.0000+00    -2.6348+01     -1.4363+02     -9.4010+01     -2.6398+02
 MNCO3             1.0000+00     1.0000+00    -2.7806+01     -9.1929+01     -9.4010+01     -2.1374+02
 NA2CO3            1.0000+00     1.0000+00    -7.2838+01     -1.0287+02     -9.4010+01     -2.6972+02
 NICO3             1.0000+00     1.0000+00    -1.1704+01     -5.7264+01     -9.4010+01     -1.6298+02
 PBCO3             1.0000+00     1.0000+00    -2.0854+01     -5.2367+01     -9.4010+01     -1.6723+02
 SRCO3             1.0000+00     1.0000+00    -5.6235+01     -1.4074+02     -9.4010+01     -2.9098+02
 ZNCO3             1.0000+00     1.0000+00    -1.6291+01     -8.3376+01     -9.4010+01     -1.9368+02
 ( AL+3)2(  CO3)3  1.0000+00     3.0000+00                   -4.0016+02     -9.4010+01
 (   BE) (  CO3)   1.0000+00     1.0000+00                   -1.4303+02     -9.4010+01
 ( BI+3)2(  CO3)3  1.0000+00     3.0000+00                   -1.3808+02     -9.4010+01
 ( CE+4) (  CO3)2  1.0000+00     2.0000+00                   -2.3293+02     -9.4010+01
 CS2CO3            1.0000+00     1.0000+00    -1.0461+02     -7.5851+01     -9.4010+01     -2.7447+02
 ( CU+1)2(  CO3)   1.0000+00     1.0000+00                   -4.0780+01     -9.4010+01
 ( FE+3)2(  CO3)3  1.0000+00     3.0000+00                   -1.9642+02     -9.4010+01
 ( MN+3)2(  CO3)3  1.0000+00     3.0000+00                   -2.2911+02     -9.4010+01
 RB2CO3            1.0000+00     1.0000+00    -9.6633+01     -7.8837+01     -9.4010+01     -2.6948+02
 ( SB+3)2(  CO3)3  1.0000+00     3.0000+00                   -1.6990+02     -9.4010+01
 ( SN+4) (  CO3)2  1.0000+00     2.0000+00                   -1.3875+02     -9.4010+01
 ( TH+4) (  CO3)2  1.0000+00     2.0000+00                   -2.9409+02     -9.4010+01
 (  U+4) (  CO3)2  1.0000+00     2.0000+00                   -2.5897+02     -9.4010+01
 ( ZR+4) (  CO3)2  1.0000+00     2.0000+00                   -2.6136+02     -9.4010+01


 AG2SO4            1.0000+00     1.0000+00    -6.8646+01     -7.3008+00     -9.4413+01     -1.7036+02
 BASO4             1.0000+00     1.0000+00    -1.2350+02     -1.3207+02     -9.4413+01     -3.4999+02
 CASO4             1.0000+00     1.0000+00    -9.4055+01     -1.5173+02     -9.4413+01     -3.4019+02
 CDSO4             1.0000+00     1.0000+00    -6.5602+01     -6.1182+01     -9.4413+01     -2.2120+02
 (   CO) (  SO4)   1.0000+00     1.0000+00                   -5.7073+01     -9.4413+01
 CUSO4             1.0000+00     1.0000+00    -5.0312+01     -3.9490+01     -9.4413+01     -1.8422+02
```

```
FESO4             1.0000+00     1.0000+00     -6.2233+01     -6.3762+01     -9.4413+01     -2.2041+02
K2SO4             1.0000+00     1.0000+00     -1.6157+02     -8.6362+01     -9.4413+01     -3.4234+02
LI2SO4            1.0000+00     1.0000+00     -1.0567+02     -1.4250+02     -9.4413+01     -3.4258+02
MGSO4             1.0000+00     1.0000+00     -6.7460+01     -1.4363+02     -9.4413+01     -3.0550+02
MNSO4             1.0000+00     1.0000+00     -6.7609+01     -9.1929+01     -9.4413+01     -2.5395+02
NA2SO4            1.0000+00     1.0000+00     -1.3335+02     -1.0287+02     -9.4413+01     -3.3064+02
NISO4             1.0000+00     1.0000+00     -6.1827+01     -5.7264+01     -9.4413+01     -2.1350+02
PBSO4             1.0000+00     1.0000+00     -7.2554+01     -5.2367+01     -9.4413+01     -2.1933+02
SRSO4             1.0000+00     1.0000+00     -1.0982+02     -1.4074+02     -9.4413+01     -3.4497+02
ZNSO4             1.0000+00     1.0000+00     -5.5903+01     -8.3376+01     -9.4413+01     -2.3369+02
AL2(SO4)3         1.0000+00     3.0000+00     -1.3699+02     -4.0016+02     -9.4413+01     -8.2038+02
BESO4             1.0000+00     1.0000+00     -4.8207+01     -1.4303+02     -9.4413+01     -2.8565+02
BI2(SO4)3         1.0000+00     3.0000+00     -1.8678+02     -1.3808+02     -9.4413+01     -6.0810+02
CE(SO4)2          1.0000+00     2.0000+00     -1.3825+02     -2.3293+02     -9.4413+01     -5.6000+02
CS2SO4            1.0000+00     1.0000+00     -1.6874+02     -7.5851+01     -9.4413+01     -3.3900+02
CU2SO4            1.0000+00     1.0000+00     -4.4316+01     -4.0780+01     -9.4413+01     -1.7951+02
FE2(SO4)3         1.0000+00     3.0000+00     -1.3594+02     -1.9642+02     -9.4413+01     -6.1560+02
MN2(SO4)3         1.0000+00     3.0000+00     -1.5456+02     -2.2911+02     -9.4413+01     -6.6690+02
RB2SO4            1.0000+00     1.0000+00     -1.6694+02     -7.8837+01     -9.4413+01     -3.4019+02
SB2(SO4)3         1.0000+00     3.0000+00     -1.2106+02     -1.6990+02     -9.4413+01     -5.7420+02
SN(SO4)2          1.0000+00     2.0000+00     -6.5820+01     -1.3875+02     -9.4413+01     -3.9340+02
TH(SO4)2          1.0000+00     2.0000+00     -1.2435+02     -2.9409+02     -9.4413+01     -6.0726+02
U(SO4)2           1.0000+00     2.0000+00     -1.1521+02     -2.5897+02     -9.4413+01     -5.6300+02
ZR(SO4)2          1.0000+00     2.0000+00     -1.4683+02     -2.6136+02     -9.4413+01     -5.9701+02

(   AG)2(FE2O4)   1.0000+00     1.0000+00                    -7.3008+00     -1.9642+02
BAFE2O4           1.0000+00     1.0000+00     -2.1993+01     -1.3207+02     -1.9642+02     -3.5049+02
(   CA) (FE2O4)   1.0000+00     1.0000+00                    -1.5173+02     -1.9642+02
(   CD) (FE2O4)   1.0000+00     1.0000+00                    -6.1182+01     -1.9642+02
(   CO) (FE2O4)   1.0000+00     1.0000+00                    -5.7073+01     -1.9642+02
CUFE2O4           1.0000+00     1.0000+00     -1.5963+00     -3.9490+01     -1.9642+02     -2.3751+02
( FE+2) (FE2O4)   1.0000+00     1.0000+00                    -6.3762+01     -1.9642+02
(    K)2(FE2O4)   1.0000+00     1.0000+00                    -8.6362+01     -1.9642+02
LI2FE2O4          1.0000+00     1.0000+00     -8.4726+00     -1.4250+02     -1.9642+02     -3.4740+02
MGFE2O4           1.0000+00     1.0000+00     -9.1697+00     -1.4363+02     -1.9642+02     -3.4922+02
MNFE2O4           1.0000+00     1.0000+00     -4.6477+00     -9.1929+01     -1.9642+02     -2.9300+02
(   NA)2(FE2O4)   1.0000+00     1.0000+00                    -1.0287+02     -1.9642+02
NIFE2O4           1.0000+00     1.0000+00     -2.7721+00     -5.7264+01     -1.9642+02     -2.5646+02
(   PB) (FE2O4)   1.0000+00     1.0000+00                    -5.2367+01     -1.9642+02
(   SR) (FE2O4)   1.0000+00     1.0000+00                    -1.4074+02     -1.9642+02
(   ZN) (FE2O4)   1.0000+00     1.0000+00                    -8.3376+01     -1.9642+02
( AL+3)2(FE2O4)3  1.0000+00     3.0000+00                    -4.0016+02     -1.9642+02
(   BE) (FE2O4)  1.0000+00     1.0000+00                  -1.4303+02   -1.9642+02
( BI+3)2(FE2O4)3 1.0000+00     3.0000+00                  -1.3808+02   -1.9642+02
( CE+4) (FE2O4)2 1.0000+00     2.0000+00                  -2.3293+02   -1.9642+02
(   CS)2(FE2O4)  1.0000+00     1.0000+00                  -7.5851+01   -1.9642+02
( CU+1)2(FE2O4)  1.0000+00     1.0000+00                  -4.0780+01   -1.9642+02
( FE+3)2(FE2O4)3 1.0000+00     3.0000+00                  -1.9642+02   -1.9642+02
( MN+3)2(FE2O4)3 1.0000+00     3.0000+00                  -2.2911+02   -1.9642+02
(   RB)2(FE2O4)  1.0000+00     1.0000+00                  -7.8837+01   -1.9642+02
( SB+3)2(FE2O4)3 1.0000+00     3.0000+00                  -1.6990+02   -1.9642+02
( SN+4) (FE2O4)2 1.0000+00     2.0000+00                  -1.3875+02   -1.9642+02
( TH+4) (FE2O4)2 1.0000+00     2.0000+00                  -2.9409+02   -1.9642+02
(  U+4) (FE2O4)2 1.0000+00     2.0000+00                  -2.5897+02   -1.9642+02
( ZR+4) (FE2O4)2 1.0000+00     2.0000+00                  -2.6136+02   -1.9642+02


AG2CRO4          1.0000+00     1.0000+00     -2.3043+01   -7.3008+00   -1.4203+02   -1.7237+02
(   BA) ( CRO4)  1.0000+00     1.0000+00                  -1.3207+02   -1.4203+02
CACRO4           1.0000+00     1.0000+00     -3.5692+01   -1.5173+02   -1.4203+02   -3.2944+02
(   CD) ( CHO4)  1.0000+00     1.0000+00                  -6.1182+01   -1.4203+02
(   CO) ( CRO4)  1.0000+00     1.0000+00                  -5.7073+01   -1.4203+02
( CU+2) ( CRO4)  1.0000+00     1.0000+00                  -3.9490+01   -1.4203+02
( FE+2) ( CRO4)  1.0000+00     1.0000+00                  -6.3762+01   -1.4203+02
(    K)2( CRO4)  1.0000+00     1.0000+00                  -8.6362+01   -1.4203+02
(   LI)2( CRO4)  1.0000+00     1.0000+00                  -1.4250+02   -1.4203+02
(   MG) ( CRO4)  1.0000+00     1.0000+00                  -1.4363+02   -1.4203+02
( MN+2) ( CRO4)  1.0000+00     1.0000+00                  -9.1929+01   -1.4203+02
NA2CRO4          1.0000+00     1.0000+00     -7.3704+01   -1.0287+02   -1.4203+02   -3.1860+02
(   NI) ( CRO4)  1.0000+00     1.0000+00                  -5.7264+01   -1.4203+02
PBCRO4           1.0000+00     1.0000+00     -2.3107+01   -5.2367+01   -1.4203+02   -2.1750+02
(   SR) ( CRO4)  1.0000+00     1.0000+00                  -1.4074+02   -1.4203+02
(   ZN) ( CRO4)  1.0000+00     1.0000+00                  -8.3376+01   -1.4203+02
( AL+3)2( CRO4)3 1.0000+00     3.0000+00                  -4.0016+02   -1.4203+02
(   BE) ( CRO4)  1.0000+00     1.0000+00                  -1.4303+02   -1.4203+02
( BI+3)2( CRO4)3 1.0000+00     3.0000+00                  -1.3808+02   -1.4203+02
( CE+4) ( CRO4)2 1.0000+00     2.0000+00                  -2.3293+02   -1.4203+02
(   CS)2( CRO4)  1.0000+00     1.0000+00                  -7.5851+01   -1.4203+02
( CU+1)2( CRO4)  1.0000+00     1.0000+00                  -4.0780+01   -1.4203+02
( FE+3)2( CRO4)3 1.0000+00     3.0000+00                  -1.9642+02   -1.4203+02
( MN+3)2( CRO4)3 1.0000+00     3.0000+00                  -2.2911+02   -1.4203+02
(   RB)2( CRO4)  1.0000+00     1.0000+00                  -7.8837+01   -1.4203+02
( SB+3)2( CRO4)3 1.0000+00     3.0000+00                  -1.6990+02   -1.4203+02
( SN+4) ( CRO4)2 1.0000+00     2.0000+00                  -1.3875+02   -1.4203+02
( TH+4) ( CRO4)2 1.0000+00     2.0000+00                  -2.9409+02   -1.4203+02
(  U+4) ( CRO4)2 1.0000+00     2.0000+00                  -2.5897+02   -1.4203+02
( ZR+4) ( CRO4)2 1.0000+00     2.0000+00                  -2.6136+02   -1.4203+02


(   AG)2( V206)  1.0000+00     1.0000+00                  -7.3008+00   -3.7268+02
(   BA) ( V206)  1.0000+00     1.0000+00                  -1.3207+02   -3.7268+02
CAV206           1.0000+00     1.0000+00     -3.4291+01   -1.5173+02   -3.7268+02   -5.5870+02
(   CD) ( V206)  1.0000+00     1.0000+00                  -6.1182+01   -3.7268+02
(   CO) ( V206)  1.0000+00     1.0000+00                  -5.7073+01   -3.7268+02
( CU+2) ( V206)  1.0000+00     1.0000+00                  -3.9490+01   -3.7268+02
( FE+2) ( V206)  1.0000+00     1.0000+00                  -6.3762+01   -3.7268+02
(    K)2( V206)  1.0000+00     1.0000+00                  -8.6362+01   -3.7268+02
(   LI)2( V206)  1.0000+00     1.0000+00                  -1.4250+02   -3.7268+02
MGV206           1.0000+00     1.0000+00     -1.1589+01   -1.4363+02   -3.7268+02   -5.2790+02
( MN+2) ( V206)  1.0000+00     1.0000+00                  -9.1929+01   -3.7268+02
NA2V206          1.0000+00     1.0000+00     -7.7386+01   -1.0287+02   -3.7268+02   -5.5294+02
(   NI) ( V206)  1.0000+00     1.0000+00                  -5.7264+01   -3.7268+02
(   PB) ( V206)  1.0000+00     1.0000+00                  -5.2367+01   -3.7268+02
(   SR) ( V206)  1.0000+00     1.0000+00                  -1.4074+02   -3.7268+02
(   ZN) ( V206)  1.0000+00     1.0000+00                  -9.3376+01   -3.7268+02
( AL+3)2( V206)3 1.0000+00     3.0000+00                  -4.0016+02   -3.7268+02
(   BE) ( V206)  1.0000+00     1.0000+00                  -1.4303+02   -3.7268+02
( BI+3)2( V206)3 1.0000+00     3.0000+00                  -1.3808+02   -3.7268+02
( CE+4) ( V206)2 1.0000+00     2.0000+00                  -2.3293+02   -3.7268+02
(   CS)2( V206)  1.0000+00     1.0000+00                  -7.5851+01   -3.7268+02
( CU+1)2( V206)  1.0000+00     1.0000+00                  -4.0780+01   -3.7268+02
( FE+3)2( V206)3 1.0000+00     3.0000+00                  -1.9642+02   -3.7268+02
( MN+3)2( V206)3 1.0000+00     3.0000+00                  -2.2911+02   -3.7268+02
(   RB)2( V206)  1.0000+00     1.0000+00                  -7.8837+01   -3.7268+02
( SB+3)2( V206)3 1.0000+00     3.0000+00                  -1.6990+02   -3.7268+02
( SN+4) ( V206)2 1.0000+00     2.0000+00                  -1.3875+02   -3.7268+02
( TH+4) ( V206)2 1.0000+00     2.0000+00                  -2.9409+02   -3.7268+02
(  U+4) ( V206)2 1.0000+00     2.0000+00                  -2.5897+02   -3.7268+02
( ZR+4) ( V206)2 1.0000+00     2.0000+00                  -2.6136+02   -3.7268+02


AG2SO3           1.0000+00     1.0000+00     -3.6170+01   -7.3008+00   -7.0929+01   -1.1440+02
BASO3            1.0000+00     1.0000+00     -7.9597+01   -1.3207+02   -7.0929+01   -2.8260+02
CASO3            1.0000+00     1.0000+00     -5.3227+01   -1.5173+02   -7.0929+01   -2.7588+02
CDSO3            1.0000+00     1.0000+00     -3.1788+01   -6.1182+01   -7.0929+01   -1.6390+02
(   CO) (   SO3) 1.0000+00     1.0000+00                  -5.7073+01   -7.0929+01
( CU+2) (   SO3) 1.0000+00     1.0000+00                  -3.9490+01   -7.0929+01
( FE+2) (   SO3) 1.0000+00     1.0000+00                  -6.3762+01   -7.0929+01
```

```
K2SO3              1.0000+00     1.0000+00    -1.0961+02    -8.6362+01    -7.0929+01    -2.6690+02
LI2SO3             1.0000+00     1.0000+00    -6.5967+01    -1.4250+02    -7.0929+01    -2.7940+02
MGSO3              1.0000+00     1.0000+00    -2.6444+01    -1.4363+02    -7.0929+01    -2.4100+02
MNSO3              1.0000+00     1.0000+00    -3.4512+01    -9.1929+01    -7.0929+01    -1.9737+02
NA2SO3             1.0000+00     1.0000+00    -8.6601+01    -1.0287+02    -7.0929+01    -2.6040+02
(    NI) (   SO3)  1.0000+00     1.0000+00                  -5.7264+01    -7.0929+01
PBSO3              1.0000+00     1.0000+00    -3.3704+01    -5.2367+01    -7.0929+01    -1.5700+02
SRSO3              1.0000+00     1.0000+00    -6.7735+01    -1.4074+02    -7.0929+01    -2.7940+02
(    ZN) (   SO3)  1.0000+00     1.0000+00                  -8.3376+01    -7.0929+01
( AL+3)2(   SO3)3  1.0000+00     3.0000+00                  -4.0016+02    -7.0929+01
(    BE) (   SO3)  1.0000+00     1.0000+00                  -1.4303+02    -7.0929+01
( BI+3)2(   SO3)3  1.0000+00     3.0000+00                  -1.3808+02    -7.0929+01
( CE+4) (   SO3)2  1.0000+00     2.0000+00                  -2.3293+02    -7.0929+01
(    CS)2(   SO3)  1.0000+00     1.0000+00                  -7.5851+01    -7.0929+01
( CU+1)2(   SO3)   1.0000+00     1.0000+00                  -4.0780+01    -7.0929+01
( FE+3)2(   SO3)3  1.0000+00     3.0000+00                  -1.9642+02    -7.0929+01
( MN+3)2(   SO3)3  1.0000+00     3.0000+00                  -2.2911+02    -7.0929+01
(    RB)2(   SO3)  1.0000+00     1.0000+00                  -7.8837+01    -7.0929+01
( SB+3)2(   SO3)3  1.0000+00     3.0000+00                  -1.6990+02    -7.0929+01
( SN+4) (   SO3)2  1.0000+00     2.0000+00                  -1.3875+02    -7.0929+01
( TH+4) (   SO3)2  1.0000+00     2.0000+00                  -2.9409+02    -7.0929+01
(   U+4) (   SO3)2 1.0000+00     2.0000+00                  -2.5897+02    -7.0929+01
( ZR+4) (   SO3)2  1.0000+00     2.0000+00                  -2.6136+02    -7.0929+01


(    AG)2( TIO3)   1.0000+00     1.0000+00                  -7.3008+00    -2.2550+02
(    BA) ( TIO3)   1.0000+00     1.0000+00                  -1.3207+02    -2.2550+02
(    CA) ( TIO3)   1.0000+00     1.0000+00                  -1.5173+02    -2.2550+02
(    CD) ( TIO3)   1.0000+00     1.0000+00                  -6.1182+01    -2.2550+02
COTIO3             1.0000+00     1.0000+00    -6.8891+00    -5.7073+01    -2.2550+02    -2.8946+02
( CU+2) ( TIO3)    1.0000+00     1.0000+00                  -3.9490+01    -2.2550+02
( FE+2) ( TIO3)    1.0000+00     1.0000+00                  -6.3762+01    -2.2550+02
(     K)2( TIO3)   1.0000+00     1.0000+00                  -8.6362+01    -2.2550+02
(    LI)2( TIO3)   1.0000+00     1.0000+00                  -1.4250+02    -2.2550+02
MGTIO3             1.0000+00     1.0000+00    -2.3756+00    -1.4363+02    -2.2550+02    -3.7150+02
( MN+2) ( TIO3)    1.0000+00     1.0000+00                  -9.1929+01    -2.2550+02
(    NA)2( TIO3)   1.0000+00     1.0000+00                  -1.0287+02    -2.2550+02
NITIO3             1.0000+00     1.0000+00    -4.9880+00    -5.7264+01    -2.2550+02    -2.8775+02
(    PB) ( TIO3)   1.0000+00     1.0000+00                  -5.2367+01    -2.2550+02
(    SR) ( TIO3)   1.0000+00     1.0000+00                  -1.4074+02    -2.2550+02
ZNTIO3             1.0000+00     1.0000+00    -3.9620-01    -8.3376+01    -2.2550+02    -3.0927+02
( AL+3)2( TIO3)3   1.0000+00     3.0000+00                  -4.0016+02    -2.2550+02
(    BE) ( TIO3)   1.0000+00     1.0000+00                  -1.4303+02    -2.2550+02
( BI+3)2( TIO3)3 1.0000+00     3.0000+00                     -1.3808+02   -2.2550+02
( CE+4) ( TIO3)2 1.0000+00     2.0000+00                     -2.3293+02   -2.2550+02
(    CS)2( TIO3)  1.0000+00     1.0000+00                     -7.5851+01   -2.2550+02
( CU+1)2( TIO3)  1.0000+00     1.0000+00                     -4.0780+01   -2.2550+02
( FE+3)2( TIO3)3 1.0000+00     3.0000+00                     -1.9642+02   -2.2550+02
( MN+3)2( TIO3)3 1.0000+00     3.0000+00                     -2.2911+02   -2.2550+02
(    RB)2( TIO3)  1.0000+00     1.0000+00                     -7.8837+01   -2.2550+02
( SB+3)2( TIO3)3 1.0000+00     3.0000+00                     -1.6990+02   -2.2550+02
( SN+4) ( TIO3)2 1.0000+00     2.0000+00                     -1.3875+02   -2.2550+02
( TH+4) ( TIO3)2 1.0000+00     2.0000+00                     -2.9409+02   -2.2550+02
(   U+4) ( TIO3)2 1.0000+00     2.0000+00                     -2.5897+02   -2.2550+02
( ZR+4) ( TIO3)2 1.0000+00     2.0000+00                     -2.6136+02   -2.2550+02

AG2WO4            1.0000+00     1.0000+00     -2.1939+01     -7.3008+00   -2.0146+02   -2.3070+02
BAWO4             1.0000+00     1.0000+00     -7.2597+01     -1.3207+02   -2.0146+02   -4.0613+02
(    CA) (  WO4)  1.0000+00     1.0000+00                     -1.5173+02   -2.0146+02
(    CD) (  WO4)  1.0000+00     1.0000+00                     -6.1182+01   -2.0146+02
(    CO) (  WO4)  1.0000+00     1.0000+00                     -5.7073+01   -2.0146+02
( CU+2) (  WO4)  1.0000+00     1.0000+00                     -3.9490+01   -2.0146+02
( FE+2) (  WO4)  1.0000+00     1.0000+00                     -6.3762+01   -2.0146+02
(     K)2(  WO4)  1.0000+00     1.0000+00                     -8.6362+01   -2.0146+02
(    LI)2(  WO4)  1.0000+00     1.0000+00                     -1.4250+02   -2.0146+02
MGWO4             1.0000+00     1.0000+00     -2.8343+01     -1.4363+02   -2.0146+02   -3.7343+02
MNWO4             1.0000+00     1.0000+00     -1.9201+01     -9.1929+01   -2.0146+02   -3.1259+02
NA2WO4            1.0000+00     1.0000+00     -7.8270+01     -1.0287+02   -2.0146+02   -3.8260+02
NIWO4             1.0000+00     1.0000+00     -1.2896+01     -5.7264+01   -2.0146+02   -2.7162+02
(    PB) (  WO4)  1.0000+00     1.0000+00                     -5.2367+01   -2.0146+02
SRWO4             1.0000+00     1.0000+00     -5.0504+01     -1.4074+02   -2.0146+02   -3.9270+02
(    ZN) (  WO4)  1.0000+00     1.0000+00                     -8.3376+01   -2.0146+02
( AL+3)2(  WO4)3 1.0000+00     3.0000+00                     -4.0016+02   -2.0146+02
(    BE) (  WO4)  1.0000+00     1.0000+00                     -1.4303+02   -2.0146+02
( BI+3)2(  WO4)3 1.0000+00     3.0000+00                     -1.3808+02   -2.0146+02
( CE+4) (  WO4)2 1.0000+00     2.0000+00                     -2.3293+02   -2.0146+02
(    CS)2(  WO4)  1.0000+00     1.0000+00                     -7.5851+01   -2.0146+02
( CU+1)2(  WO4)  1.0000+00     1.0000+00                     -4.0780+01   -2.0146+02
( FE+3)2(  WO4)3 1.0000+00     3.0000+00                     -1.9642+02   -2.0146+02
( MN+3)2(  WO4)3 1.0000+00     3.0000+00                     -2.2911+02   -2.0146+02
(    RB)2(  WO4)  1.0000+00     1.0000+00                     -7.8837+01   -2.0146+02
( SB+3)2(  WO4)3 1.0000+00     3.0000+00                     -1.6990+02   -2.0146+02
( SN+4) (  WO4)2 1.0000+00     2.0000+00                     -1.3875+02   -2.0146+02
( TH+4) (  WO4)2 1.0000+00     2.0000+00                     -2.9409+02   -2.0146+02
(   U+4) (  WO4)2 1.0000+00     2.0000+00                     -2.5897+02   -2.0146+02
( ZR+4) (  W04)2 1.0000+00     2.0000+00                  -2.6136+02    -2.0146+02

AG2M004          1.0000+00     1.0000+00    -3.1414+01    -7.3008+00    -1.7788+02    -2.1660+02
(    BA) ( M004) 1.0000+00     1.0000+00                  -1.3207+02    -1.7788+02
(    CA) ( M004) 1.0000+00     1.0000+00                  -1.5173+02    -1.7788+02
(    CD) ( M004) 1.0000+00     1.0000+00                  -6.1182+01    -1.7788+02
(    CO) ( M004) 1.0000+00     1.0000+00                  -5.7073+01    -1.7788+02
( CU+2) ( M004)  1.0000+00     1.0000+00                  -3.9490+01    -1.7788+02
( FE+2) ( M004)  1.0000+00     1.0000+00                  -6.3762+01    -1.7788+02
(     K)2( M004) 1.0000+00     1.0000+00                  -8.6362+01    -1.7788+02
(    LI)2( M004) 1.0000+00     1.0000+00                  -1.4250+02    -1.7788+02
(    MG) ( M004) 1.0000+00     1.0000+00                  -1.4363+02    -1.7788+02
( MN+2) ( M004)  1.0000+00     1.0000+00                  -9.1929+01    -1.7788+02
NA2M004          1.0000+00     1.0000+00    -7.3295+01    -1.0287+02    -1.7788+02    -3.5405+02
(    NI) ( M004) 1.0000+00     1.0000+00                  -5.7264+01    -1.7788+02
PBM004           1.0000+00     1.0000+00    -3.5398+01    -5.2367+01    -1.7788+02    -2.6565+02
(    SR) ( M004) 1.0000+00     1.0000+00                  -1.4074+02    -1.7788+02
(    ZN) ( M004) 1.0000+00     1.0000+00                  -8.3376+01    -1.7788+02
( AL+3)2( M004)3 1.0000+00     3.0000+00                  -4.0016+02    -1.7788+02
(    BE) ( M004) 1.0000+00     1.0000+00                  -1.4303+02    -1.7788+02
( BI+3)2( M004)3 1.0000+00     3.0000+00                  -1.3808+02    -1.7788+02
( CE+4) ( M004)2 1.0000+00     2.0000+00                  -2.3293+02    -1.7788+02
(    CS)2( M004) 1.0000+00     1.0000+00                  -7.5851+01    -1.7788+02
( CU+1)2( M004)  1.0000+00     1.0000+00                  -4.0780+01    -1.7788+02
( FE+3)2( M004)3 1.0000+00     3.0000+00                  -1.9642+02    -1.7788+02
( MN+3)2( M004)3 1.0000+00     3.0000+00                  -2.2911+02    -1.7788+02
(    RB)2( M004) 1.0000+00     1.0000+00                  -7.8837+01    -1.7788+02
( SB+3)2( M004)3 1.0000+00     3.0000+00                  -1.6990+02    -1.7788+02
( SN+4) ( M004)2 1.0000+00     2.0000+00                  -1.3875+02    -1.7788+02
( TH+4) ( M004)2 1.0000+00     2.0000+00                  -2.9409+02    -1.7788+02
(   U+4) ( M004)2 1.0000+00    2.0000+00                  -2.5897+02    -1.7788+02
( ZR+4) ( M004)2 1.0000+00     2.0000+00                  -2.6136+02    -1.7788+02


(    AG)2(AL204) 1.0000+00     1.0000+00                  -7.3008+00    -4.0016+02
(    BA) (AL204) 1.0000+00     1.0000+00                  -1.3207+02    -4.0016+02
(    CA) (AL204) 1.0000+00     1.0000+00                  -1.5173+02    -4.0016+02
(    CD) (AL204) 1.0000+00     1.0000+00                  -6.1182+01    -4.0016+02
COAL204          1.0000+00     1.0000+00    -9.2993+00    -5.7073+01    -4.0016+02    -4.6653+02
( CU+2) (AL204)  1.0000+00     1.0000+00                  -3.9490+01    -4.0016+02
FEAL204          1.0000+00     1.0000+00    -1.0480+01    -6.3762+01    -4.0016+02    -4.7440+02
(     K)2(AL204) 1.0000+00     1.0000+00                  -8.6362+01    -4.0016+02
```

```
LI2AL204           1.0000+00     1.0000+00     -2.5919+01     -1.4250+02     -4.0016+02     -5.6858+02
MGAL204            1.0000+00     1.0000+00     -7.2158+00     -1.4363+02     -4.0016+02     -5.5100+02
MNAL204            1.0000+00     1.0000+00     -9.0038+00     -9.1929+01     -4.0016+02     -5.0109+02
NA2AL204           1.0000+00     1.0000+00     -3.8312+01     -1.0287+02     -4.0016+02     -5.4134+02
NIAL204            1.0000+00     1.0000+00     -5.8982+00     -5.7264+01     -4.0016+02     -4.6332+02
(   PB) (AL204)    1.0000+00     1.0000+00                    -5.2367+01     -4.0016+02
SRAL204            1.0000+00     1.0000+00     -1.8917+01     -1.4074+02     -4.0016+02     -5.5981+02
(   ZN) (AL204)    1.0000+00     1.0000+00                    -8.3376+01     -4.0016+02
( AL+3)2(AL204)3   1.0000+00     3.0000+00                    -4.0016+02     -4.0016+02
(   BE) (AL204)    1.0000+00     1.0000+00                    -1.4303+02     -4.0016+02
( BI+3)2(AL204)3   1.0000+00     3.0000+00                    -1.3808+02     -4.0016+02
( CE+4) (AL204)2   1.0000+00     2.0000+00                    -2.3293+02     -4.0016+02
(   CS)2(AL204)    1.0000+00     1.0000+00                    -7.5851+01     -4.0016+02
( CU+1)2(AL204)    1.0000+00     1.0000+00                    -4.0780+01     -4.0016+02
( FE+3)2(AL204)3   1.0000+00     3.0000+00                    -1.9642+02     -4.0016+02
( MN+3)2(AL204)3   1.0000+00     3.0000+00                    -2.2911+02     -4.0016+02
(   RB)2(AL204)    1.0000+00     1.0000+00                    -7.8837+01     -4.0016+02
( SB+3)2(AL204)3   1.0000+00     3.0000+00                    -1.6990+02     -4.0016+02
( SN+4) (AL204)2   1.0000+00     2.0000+00                    -1.3875+02     -4.0016+02
( TH+4) (AL204)2   1.0000+00     2.0000+00                    -2.9409+02     -4.0016+02
(  U+4) (AL204)2   1.0000+00     2.0000+00                    -2.5897+02     -4.0016+02
( ZR+4) (AL204)2   1.0000+00     2.0000+00                    -2.6136+02     -4.0016+02
```

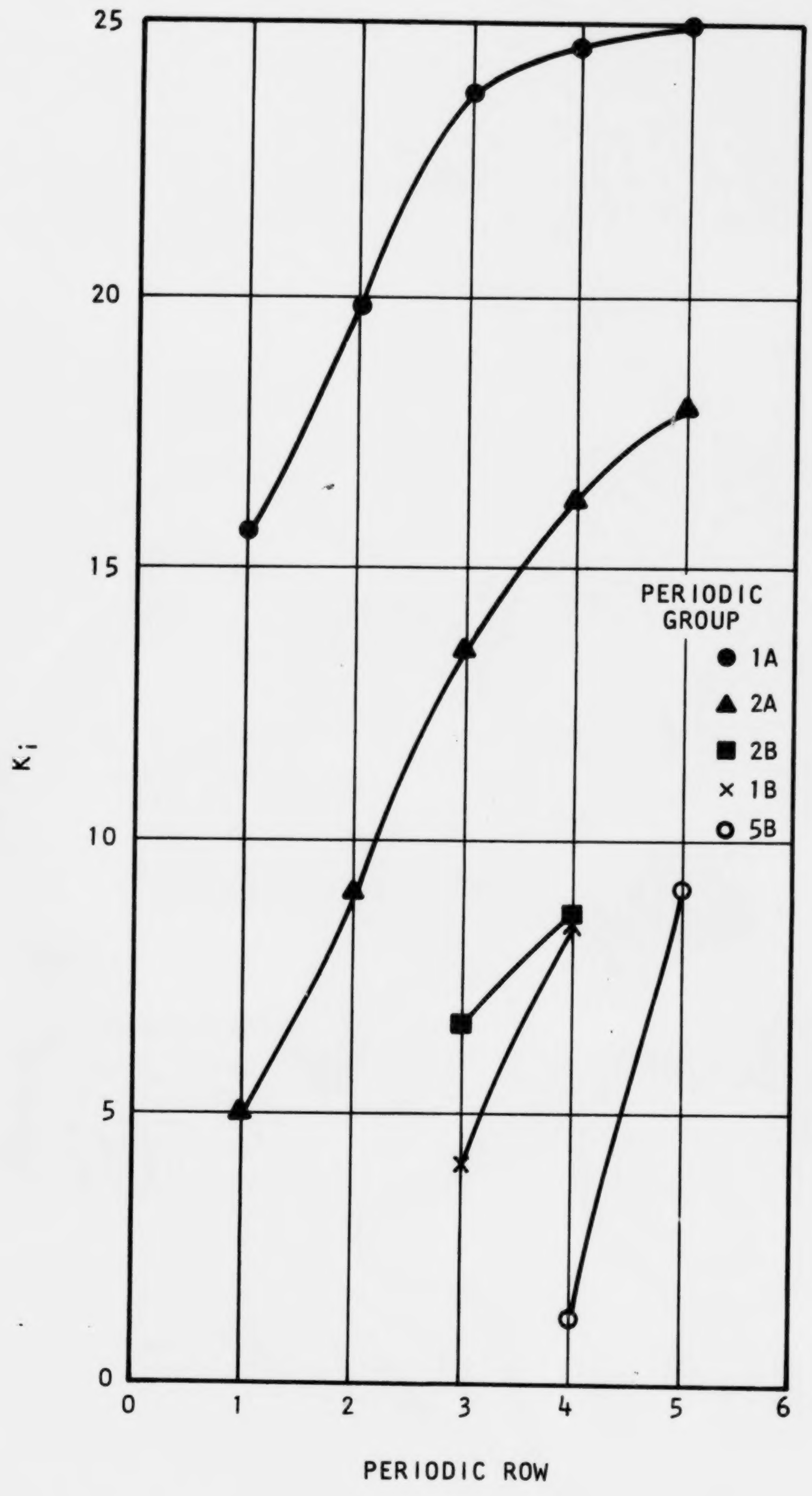


FIG. 1 - CATION COMBINING POWER

TRACOR DWG. A6-3-896
10/14/68 PARSON

REFERENCES

Pa-1 Pauling, L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, (1960).

Er-1 Erdős, E., "Thermo Properties of Sulfites," Coll. Czech. Chemical Commun., Prague 27, 1428-37, (1962).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

2 May 1968 T. Parsons

TECHNICAL MEMORANDUM 004-009-CH5

THE ESTIMATION OF STANDARD ENTROPIES FOR INORGANIC COMPOUNDS

I. INTRODUCTION AND SUMMARY

Five methods for estimating absolute entropy were investigated. All of the methods were based on the idea of adding cation and anion entropy contributions and applying a correction. Anion entropy contributions were obtained by subtracting known metal entropies from known compound entropies. The predictions of each method were compared with experimentally obtained entropies. Latimer's method was found to have the smallest RMS error. Since Latimer's method was also the most widely applicable, it was chosen to be used for the estimation of unknown entropies. Anion entropy contributions were determined from entropies in the TRACOR data base according to Latimer's method. Entropies of inorganic compounds were estimated by adding the cation contributions from Table I and the anion contributions from Table X. TRACOR anion entropy values were used when possible so that estimates would be consistent with other values in the TRACOR data base. When TRACOR values were not available Latimer's values were used. The estimated entropies were added to the TRACOR data base with a reference to this memorandum.

II. TECHNICAL DISCUSSION OF THE PROBLEM

The following study describes the selection of a method for estimating the entropy at 298.16° K of the oxides, carbonates, sulfites, sulfates, sulfides, and mixed oxides of the metals given in Table VI. With entropy values and heats of formation for such compounds one can calculate the free energy change for reactions they might undergo and thus obtain a description of the direction and extent of such reactions. Since it is not always possible to obtain experimental values for entropy of formation, absolute entropy values are calculated from Equation (1).

$$S^{\circ}_{T} = \int_{0}^{T} \frac{Cp}{T}\, dT \qquad (1)$$

Expressions for the heat capacity, Cp, are often well defined and of one general form at temperatures above 298.16° K. As the temperature approaches absolute zero, heat capacity equations become varied and complicated and inconvenient for a computer-oriented study employing a general equation for repeated calculation of hundreds of entropy and free energy values. Therefore, the following equation is used to calculate the entropy of a compound at a given temperature, T.

$$S^\circ_T = S^\circ_{298} + \int_{298}^{T} \frac{Cp}{T}\, dT \qquad (2)$$

The term S°_{298} in Equation (2) is the one of interest in this discussion since it represents information that is difficult to obtain experimentally.

All of the methods for estimating S°_{298} have a semitheoretical basis. This basis approximates the Debye crystal theory. The Debye theory takes into account the mass of the units that move and the cohesive forces holding them together. Other related physical phenomena are acoustic velocity, modules of elasticity, Poisson's ratio, etc.

The first method to be investigated is that first proposed by Latimer (La-1) in 1921 and the later modified by him in 1951 (La-2). The original article gave an equation for estimating entropies of compounds based on the masses of the atoms involved and the constraints by which they are held. Latimer stated that according to the quantum theory, the principle of dimensions, and the principle of similitude, the form of the entropy equation for solids should be:

$$S = \frac{3}{2}R \ln m + \frac{5}{2}R \ln T - R\ln P + S_o \qquad (3)$$

where S_o is a constant independent of the substance. He found that those compounds that fulfilled the assumptions of his theory usually had reached their Kopp's law value at room temperature. To extend his method from elements to compounds he used the formula:

$$S^{\circ}_{298} = \frac{3}{2}R\sum_{i=1}^{I} \ln\,(\text{atomic weight})_i + S'_o \qquad (4)$$

where there are I atoms forming the molecule. S'_o has the same value for all elements. He then chose the value 19.7 for the entropy of potassium chloride at 298.16° as the most accurate entropy value known and obtained a value of -0.94 for S'_o.

In general, Latimer took a classical equation for the entropy of a monatomic gas, imposed conditions of specific temperature and pressure, and concluded that the entropy is determined by the mass of the atoms and the number of degrees of freedom they possess. He further assumed that for solids with three degrees of freedom per atom, the constraints are limited and their effect negligible if the Kopp's Law constants of the elements are at least six. Also necessary for Latimer's method is the assumption that in compounds for which the above statements hold true, the entropies are equal to the sum of entropies of the atoms.

In 1951 Latimer (La-2) amended his estimation method in light of the fact that when ionic attractions are involved in solid salts, the entropy of a large ion is increased and that of a small ion is decreased as compared to values obtained using Equation (4). On a graph of standard entropy versus atomic weight, assuming a correlation between size and atomic weight, Latimer corrected values calculated by Equation (4) (dotted line) with the unbroken line. The resulting entropies are shown in Table I.

TABLE I

LATIMER'S ENTROPY ESTIMATIONS

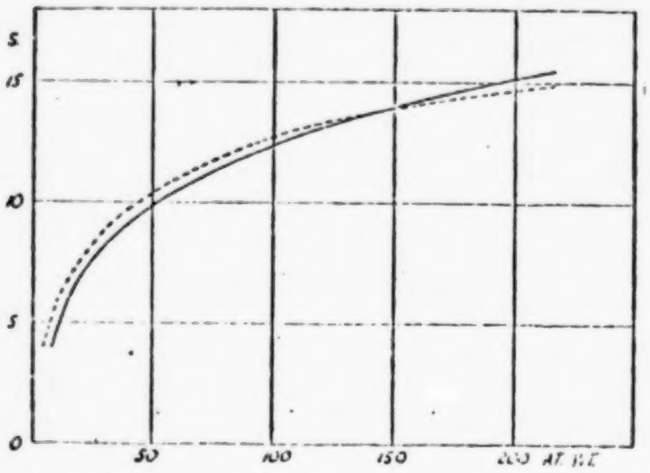


Fig. 1.--Entropies of the elements in solid compounds at 25° as a function of atomic weight: dotted line, Equation 1; full line curve used for Table I.

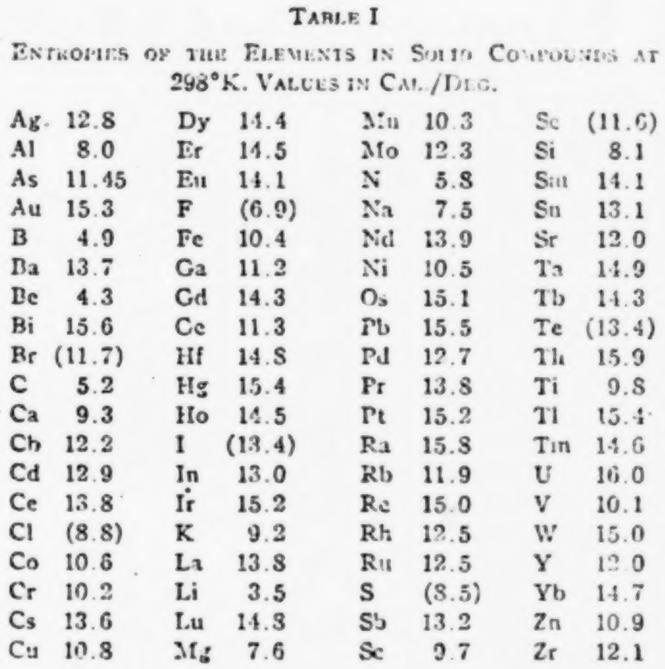


TABLE I

ENTROPIES OF THE ELEMENTS IN SOLID COMPOUNDS AT 298°K. VALUES IN CAL./DEG.

Ag	12.8	Dy	14.4	Mn	10.3	Se	(11.6)
Al	8.0	Er	14.5	Mo	12.3	Si	8.1
As	11.45	Eu	14.1	N	5.8	Sm	14.1
Au	15.3	F	(6.9)	Na	7.5	Sn	13.1
B	4.9	Fe	10.4	Nd	13.9	Sr	12.0
Ba	13.7	Ga	11.2	Ni	10.5	Ta	14.9
Be	4.3	Gd	14.3	Os	15.1	Tb	14.3
Bi	15.6	Ge	11.3	Pb	15.5	Te	(13.4)
Br	(11.7)	Hf	14.8	Pd	12.7	Th	15.9
C	5.2	Hg	15.4	Pr	13.8	Ti	9.8
Ca	9.3	Ho	14.5	Pt	15.2	Tl	15.4
Cb	12.2	I	(13.4)	Ra	15.8	Tm	14.6
Cd	12.9	In	13.0	Rb	11.9	U	16.0
Ce	13.8	Ir	15.2	Re	15.0	V	10.1
Cl	(8.8)	K	9.2	Rh	12.5	W	15.0
Co	10.6	La	13.8	Ru	12.5	Y	12.0
Cr	10.2	Li	3.5	S	(8.5)	Yb	14.7
Cs	13.6	Lu	14.8	Sb	13.2	Zn	10.9
Cu	10.8	Mg	7.6	Sc	9.7	Zr	12.1

W. Latimer, "Methods of Estimating the Entropies of Solid Compounds," J. Am. Chem. Soc., vol. 73, p. 1480 (1951)

The author had also determined empirically that the entropy of an ionic solid depends on the ionic charge. By subtracting the entropy of the cations from that of a number of chlorides, constant values were determined for the entropy of the chloride ion when combined with +1, +2, or +3-charged cations. From such data for many negative ions, Latimer concluded that it was more accurate to use different entropy values for each anion when it was combined with +1, +2, or +3-charged cations. Table II was the result of these conclusions.

TABLE II

LATIMER'S ANION ENTROPY CONTRIBUTIONS

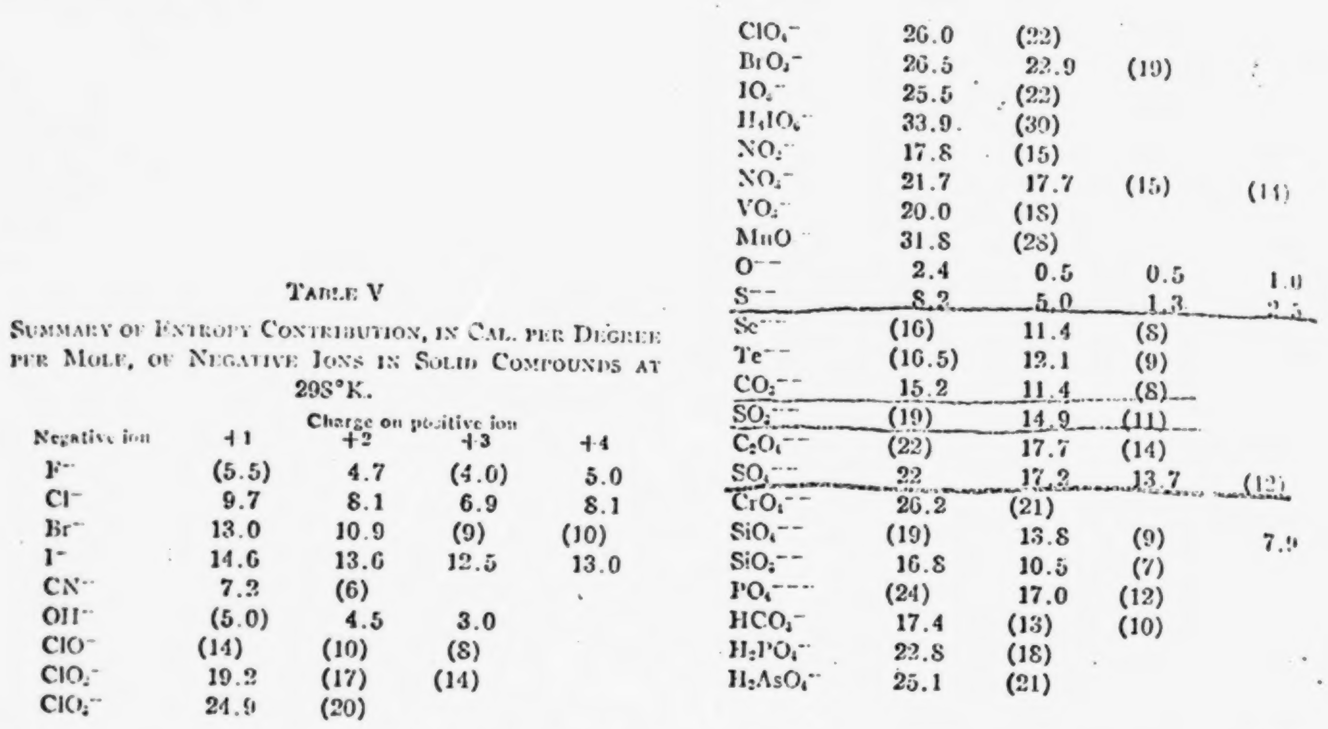


TABLE V

SUMMARY OF ENTROPY CONTRIBUTION, IN CAL. PER DEGREE PER MOLE, OF NEGATIVE IONS IN SOLID COMPOUNDS AT 298°K.

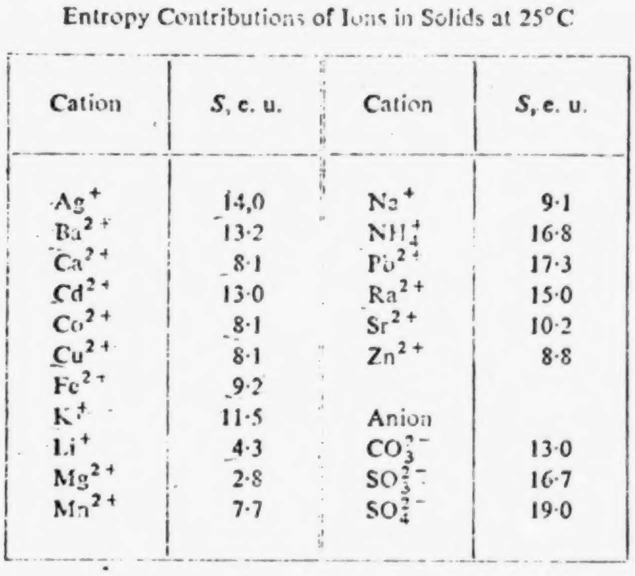
Negative ion	Charge on positive ion +1	+2	+3	+4
F^-	(5.5)	4.7	(4.0)	5.0
Cl^-	9.7	8.1	6.9	8.1
Br^-	13.0	10.9	(9)	(10)
I^-	14.6	13.6	12.5	13.0
CN^-	7.2	(6)		
OH^-	(5.0)	4.5	3.0	
ClO^-	(14)	(10)	(8)	
ClO_2^-	19.2	(17)	(14)	
ClO_3^-	24.9	(20)		
ClO_4^-	26.0	(22)		
BrO_3^-	26.5	22.9	(19)	
IO_3^-	25.5	(22)		
$H_4IO_6^-$	33.9	(30)		
NO_2^-	17.8	(15)		
NO_3^-	21.7	17.7	(15)	(14)
VO_3^-	20.0	(18)		
MnO_4^-	31.8	(28)		
O^{--}	2.4	0.5	0.5	1.0
S^{--}	8.2	5.0	1.3	2.5
Se^{--}	(16)	11.4	(8)	
Te^{--}	(16.5)	12.1	(9)	
CO_3^{--}	15.2	11.4	(8)	
SO_3^{--}	(19)	14.9	(11)	
$C_2O_4^{--}$	(22)	17.7	(14)	
SO_4^{--}	22	17.2	13.7	(12)
CrO_4^{--}	26.2	(21)		
SiO_4^{--}	(19)	13.8	(9)	7.9
SiO_3^{--}	16.8	10.5	(7)	
PO_4^{---}	(24)	17.0	(12)	
HCO_3^-	17.4	(13)	(10)	
$H_2PO_4^-$	22.8	(18)		
$H_2AsO_4^-$	25.1	(21)		

W. Latimer, "Methods of Estimating the Entropies of Solid Compounds", J. Am. Chem. Soc., vol. 73, p. 1480 (1951).

The second method of estimation of entropies to be examined is that presented by E. Erdős (Er-1). Erdős gave no theoretical support to his method. Instead he described it as modification of Latimer's method which gave more accurate results. He maintained that a constant entropy contribution should be assigned to each ion regardless of the charge on the other ion and that such a procedure resulted in a much smaller deviation of calculated values compared to observed. He used the experimentally obtained entropy of a carbonate compound as a basis for all other calculations. By the method of subtracting estimated elemental entropies from entropies of compounds he obtained the entropies of sulfites, sulfates, and carbonates. Results of Erdős' investigations are shown in Table III.

TABLE III

ERDÖS' ENTROPY ESTIMATIONS



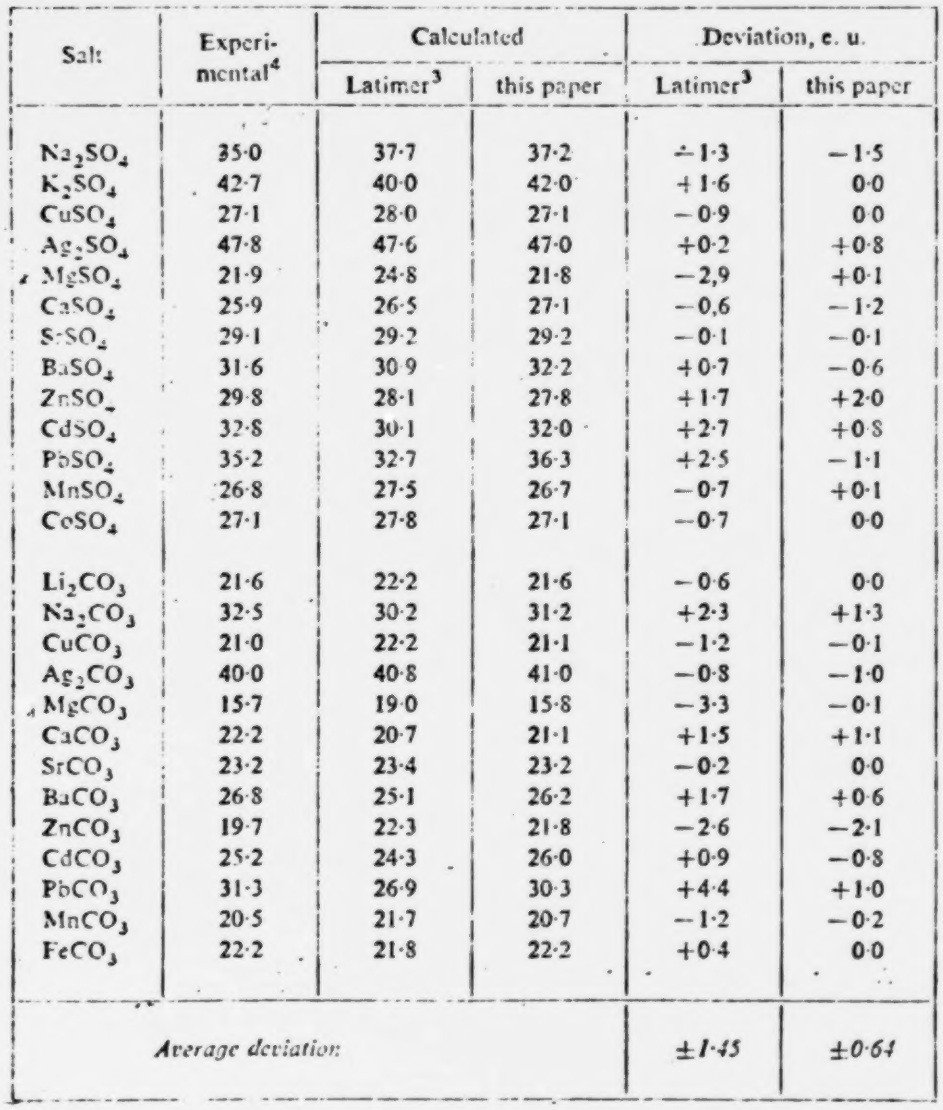
Entropy Contributions of Ions in Solids at 25°C

Cation	*S*, e. u.	Cation	*S*, e. u.
Ag^+	14,0	Na^+	9·1
Ba^{2+}	13·2	NH_4^+	16·8
Ca^{2+}	8·1	Pb^{2+}	17·3
Cd^{2+}	13·0	Ra^{2+}	15·0
Co^{2+}	8·1	Sr^{2+}	10·2
Cu^{2+}	8·1	Zn^{2+}	8·8
Fe^{2+}	9·2		
K^+	11·5	Anion	
Li^+	4·3	CO_3^{2-}	13·0
Mg^{2+}	2·8	SO_3^{2-}	16·7
Mn^{2+}	7·7	SO_4^{2-}	19·0

E. Erdős, "Thermodynamic Properties of Sulfites, II. Absolute Entropies, Heat Capacities, and Dissociation Pressures", Coll. Czech. Chem. Commun., vol. 27, p. 2273 (1962).

TABLE III
ERDÖS' ENTROPY ESTIMATIONS

Absolute Entropies S^0 in cal/grad.mol of Sulphates and Carbonates at 25°C



Salt	Experimental[4]	Calculated		Deviation, e. u.	
		Latimer[3]	this paper	Latimer[3]	this paper
Na_2SO_4	35·0	37·7	37·2	−1·3	−1·5
K_2SO_4	42·7	40·0	42·0	+1·6	0·0
$CuSO_4$	27·1	28·0	27·1	−0·9	0·0
Ag_2SO_4	47·8	47·6	47·0	+0·2	+0·8
$MgSO_4$	21·9	24·8	21·8	−2,9	+0·1
$CaSO_4$	25·9	26·5	27·1	−0,6	−1·2
$SrSO_4$	29·1	29·2	29·2	−0·1	−0·1
$BaSO_4$	31·6	30·9	32·2	+0·7	−0·6
$ZnSO_4$	29·8	28·1	27·8	+1·7	+2·0
$CdSO_4$	32·8	30·1	32·0	+2·7	+0·8
$PbSO_4$	35·2	32·7	36·3	+2·5	−1·1
$MnSO_4$	26·8	27·5	26·7	−0·7	+0·1
$CoSO_4$	27·1	27·8	27·1	−0·7	0·0
Li_2CO_3	21·6	22·2	21·6	−0·6	0·0
Na_2CO_3	32·5	30·2	31·2	+2·3	+1·3
$CuCO_3$	21·0	22·2	21·1	−1·2	−0·1
Ag_2CO_3	40·0	40·8	41·0	−0·8	−1·0
$MgCO_3$	15·7	19·0	15·8	−3·3	−0·1
$CaCO_3$	22·2	20·7	21·1	+1·5	+1·1
$SrCO_3$	23·2	23·4	23·2	−0·2	0·0
$BaCO_3$	26·8	25·1	26·2	+1·7	+0·6
$ZnCO_3$	19·7	22·3	21·8	−2·6	−2·1
$CdCO_3$	25·2	24·3	26·0	+0·9	−0·8
$PbCO_3$	31·3	26·9	30·3	+4·4	+1·0
$MnCO_3$	20·5	21·7	20·7	−1·2	−0·2
$FeCO_3$	22·2	21·8	22·2	+0·4	0·0
Average deviation				*±1·45*	*±0·64*

E. Erdős, "Thermodynamic Properties of Sulfites, II. Absolute Entropies, Heat Capacities, and Dissociation Pressures", Coll. Czech. Chem. Commun., vol. 27, p. 2273 (1962).

The third method of calculation of absolute entropies is that of N. N. Drozin (Dr-1). Drozin used Berthelot's Principle, which states that the Gibbs free energy is equal to the heat of reaction when the entropy change of the reaction is zero or insignificant. If the latter is true, then the entropy of the products is equal to that of the reactants; for example:

$$S_{NaCl}+S_{K} = S_{KCl}+S_{Na} \tag{5}$$

Rearranging Equation (6), Drozin obtained:

$$S_{NaCl}-S_{Na} = S_{KCl}-S_{K} \tag{6}$$

He then stated the following rule: "The difference in entropy between a compound and the element forming the positive ion in the compound is constant for compounds of the same type and of the same subgroup." Drozin used the principle to calculate entropies and found difficulties with those of the lighter elements. When the difference in entropy of a compound and its element in a given subgroup is not constant, as with the lighter elements, Drozin proposed that such a decrease in difference is dependent on the change in molecular volume of the compounds compared with the volume of the same type compound of elements in the same subgroup.

From the entropy equation for the distribution of Debye frequencies, Drozin derived Equation (7), (also see Davidson, Da-1), where N is Avogardo's number, V the molecular volume, and F a constant whose value depends on density, compressibility, and Poisson's ratio.

$$S = 3R \ln \frac{KTV^{2/3}F^{2/3}}{h(3N)^{2/3}} + 4R \qquad (7)$$

From (7) Drozin showed that the difference in entropy between two substances is:

$$S_2 - S_1 = R\ln \frac{V_2}{V_1} + R\ln \frac{F_2}{F_1} \qquad (8)$$

From these considerations Drozin derived a "semi-empirical volume correction" using $MgCO_3$ and $BaCO_3$ as an example:

$$S_{MgCO_3,exp} = S_{BaCO_3} - S_{Ba} + S_{Mg} - \Delta S_v \qquad (9)$$

The ideal entropy $S_{MgCO_3,\ ideal}$ is equal to the entropy for the ideal case where the molecular volume of $MgCO_3$ is equal to that of $BaCO_3$. The ideal entropy is expressed by the first three terms on the right side of Equation (9). The volume correction is then seen to be:

$$\Delta S_v = S_{ideal} - S_{exp} \tag{10}$$

From Equation (8):

$$\Delta S_v = R \ln \frac{V_{ideal}}{V_{exp}} + R \ln \frac{F_{ideal}}{F_{exp}} \tag{11}$$

Since the volume correction doesn't usually exceed one entropy unit, Drozin ignored the F term and calculated the entropy by Equation (12).

$$S_{MgCO_3} = S_{BaCO_3} - S_{Ba} + S_{Mg} - R \ln \frac{V_{BaCO_3}}{V_{MgCO_3}} \tag{12}$$

The author pointed out, with Table IV as evidence, that when there is appreciable change in molecular volume the agreement between experimental and calculated values is not as good. ($MgCl_2$, $MgCO_3$, MgO)

The volume correction changes the average deviation from 0.76 to 0.64 e.u.

TABLE IV

Effect of volume correction on value of entropy*.

Formula used for calculation	Compound	S, e.u. (calc. without vol. correction)	S, e.u. (calc. with vol. correction)	S, e.u. (expt.)
$S_{CaSO_4} = S_{BaSO_4} - S_{Ba} +$ $+ S_{Ca} - R\ln\frac{v_{BaSO_4}}{v_{CaSO_4}}$ $S_{CaSO_4} = 31.6 - 16.0 +$ $+ 9.95 - 4.58\log\frac{46.7}{46.0}$	$CaSO_4$	25.5	25.5	25.5
$S_{ZnSO_4} = S_{CaSO_4} - S_{Ca} +$ $+ S_{Zn} - R\ln\frac{v_{CaSO_4}}{v_{ZnSO_4}}$ $S_{ZnSO_4} = 32.8 - 12.3 +$ $+ 9.95 - 4.58\log\frac{44.5}{45.6}$	$ZnSO_4$	30.5	30.6	29.8
$S_{SrCO_3} = S_{BaCO_3} - S_{Ba} +$ $+ S_{Sr} - R\ln\frac{v_{BaCO_3}}{v_{SrCO_3}}$ $S_{SrCO_3} = 20.8 - 16.0 +$ $+ 13.0 - 4.58\log\frac{45.0}{41.7}$	$SrCO_3$	23.8	23.6	23.2
$S_{MgCl_2} = S_{BaCl_2} - S_{Ba} +$ $+ S_{Mg} - R\ln\frac{v_{BaCl_2}}{v_{MgCl_2}}$ $S_{MgCl_2} = 30.0 - 16.0 +$ $+ 7.77 - 4.58\log\frac{54.3}{41.0}$	$MgCl_2$	21.8	21.2	21.4
$S_{MgCO_3} = S_{BaCO_3} - S_{Ba} +$ $+ S_{Mg} - R\ln\frac{v_{BaCO_3}}{v_{MgCO_3}}$ $S_{MgCO_3} = 26.8 - 16.0 +$ $+ 7.77 - 4.58\log\frac{45.0}{28.0}$	$MgCO_3$	18.6	17.6	15.7
$S_{SiO_2} = S_{GeO_2} - S_{Ge} +$ $+ S_{Si} - R\ln\frac{v_{GeO_2}}{v_{SiO_2}}$ $S_{SiO_2} = 10.8[3] - 7.43[3] +$ $+ 4.47 - 4.58\log\frac{22.2}{25.9}$	SiO_2	7.8	8.1	10.0
$S_{GeO_2} = S_{PbO_2} - S_{Pb} + S_{Ge} -$ $- R\ln\frac{v_{PbO_2}}{v_{GeO_2}}$ $S_{GeO_2} = 18.3 - 15.51 +$ $+ 7.43 - 4.58\log\frac{25.5}{22.2}$	GeO_2	10.2	9.9	10.8*
$S_{Al_2O_3} = S_{In_2O_3} - 2S_{In} +$ $+ 2S_{Al} - R\ln\frac{v_{In_2O_3}}{v_{Al_2O_3}}$ $S_{Al_2O_3} = 27.0[3] - 2\cdot 13.82[3] +$ $+ 28.77 - 4.58\log\frac{38.6}{25.5}$	Al_2O_3	12.9	12.1	12.19
$S_{Al_2O_3} = S_{Ga_2O_3} - 2S_{Ga} +$ $+ 2S_{Al} - R\ln\frac{v_{Ga_2O_3}}{v_{Al_2O_3}}$ $S_{Al_2O_3} = 20.31[3] - 2\cdot 9.82[3] +$ $+ 26.77 - 4.58\log\frac{29.0}{25.5}$	Al_2O_3	14.2	13.9	12.19
$S_{MgO} = S_{CaO} - S_{Ca} +$ $+ S_{Mg} - R\ln\frac{v_{CaO}}{v_{MgO}}$ $S_{MgO} = 9.5 - 9.95 +$ $+ 7.77 - 4.58\log\frac{16.5}{11.05}$	MgO	7.3	6.5	6.4
$S_{Na_2SO_4} = S_{K_2SO_4} - 2S_{K} +$ $+ 2S_{Na} - R\ln\frac{v_{K_2SO_4}}{v_{Na_2SO_4}}$ $S_{Na_2SO_4} = 42.0 - 2\cdot 15.2 +$ $+ 2\cdot 12.2 - 4.58\log\frac{65.5}{52.6}$	Na_2SO_4	36.0	35.8	35.7
$S_{MgF_2} = S_{CaF_2} - S_{Ca} +$ $+ S_{Mg} - R\ln\frac{v_{CaF_2}}{v_{MgF_2}}$ $S_{MgF_2} = 16.45[6] - 9.95 +$ $+ 7.77 - 4.58\log\frac{24.6}{21.1}$	MgF_2	14.3	14.0	13.68
$S_{MgF_2} = S_{BaF_2} - S_{Ba} +$ $+ S_{Mg} - R\ln\frac{v_{BaF_2}}{v_{MgF_2}}$ $S_{MgF_2} = 23.0[6] - 16.0 +$ $+ 7.77 - 4.58\log\frac{36.3}{22.1}$	MgF_2	14.8	13.7	13.68
$S_{LiF} = S_{KF} - S_{K} +$ $+ S_{Li} - R\ln\frac{v_{KF}}{v_{LiF}}$ $S_{LiF} = 15.9 - 15.2 +$ $+ 6.7 - 4.58\log\frac{23.4}{11.3}$	LiF	7.4	6.0	8.53*
$S_{LiF} = S_{NaF} - S_{Na} +$ $+ S_{Li} - R\ln\frac{v_{NaF}}{v_{LiF}}$ $S_{LiF} = 14.0 - 12.2 +$ $+ 6.7 - 4{,}58\log\frac{15.1}{11.3}$	LiF	8.5	7.9	8.53*
$S_{As_2O_3} = S_{Sb_2O_3} - 2S_{Sb} +$ $+ 2S_{As} - R\ln\frac{v_{Sb_2O_3}}{v_{As_2O_3}}$ $S_{As_2O_3} = 29.4[3] - 2\cdot 10.5[6] +$ $+ 2\cdot 8.4[6] - 4.58\log\frac{51.41}{52.92}$	As_2O_3	25.2	25.3	25.6*
$S_{As_2O_3} = S_{Bi_2O_3} - 2S_{Bi} +$ $+ 2S_{As} - R\ln\frac{v_{Bi_2O_3}}{v_{As_2O_3}}$ $S_{As_2O_3} = 36.2[6] + 2\cdot 13.6[6] +$ $+ 2\cdot 8.40 - 4.58\log\frac{54.5}{52.92}$	As_2O_3	25.8	25.2	25.6*
$S_{MoO_2} = S_{WO_2} - S_{W} +$ $+ S_{Mo} - R\ln\frac{v_{WO_2}}{v_{MoO_2}}$ $S_{MoO_2} = 19.1[3] - 7.83[3] +$ $+ 6.83[3] - 4.58\log\frac{32.4}{32.0}$	MoO_2	18.0	18.0	13.38*
$S_{Li_2CO_3} = S_{Na_2CO_3} - 2S_{Na} +$ $+ 2S_{Li} - R\ln\frac{v_{Na_2CO_3}}{v_{Li_2CO_3}}$ $S_{Li_2CO_3} = 32.5 - 2\cdot 12.2 +$ $+ 2\cdot 6.7 - 4.58\log\frac{41.8}{35.0}$	Li_2CO_3	21.5	21.1	21.6

---

* The standard entropy values for which no reference is indicated have been taken from Ref. 2. Density values required for calculation of molecular volumes have been taken from Ref. 7.

approximation, be equated to zero. The volume correction is then

$$\Delta S = R\ln\frac{v_2}{v_1}. \tag{13}$$

The final formula for calculating standard entropy becomes

$$S_{b_1a_1} = S_{b_2a_1} - S_{b_2} + S_{b_1} - R\ln\frac{v_{b_2a_1}}{v_{b_1a_1}}. \tag{14}$$

In the present example

$$S_{MgCO_3} = S_{BaCO_3} - S_{Ba} + S_{Mg} - R\ln\frac{v_{BaCO_3}}{v_{MgCO_3}}. \tag{15}$$

N. N. Drozin, "Application of Berthelot's Principle to the Calculation of Standard Entropies of Solid Inorganic Compounds", Russ. J. Phys. Chem., vol. 38, p. 1386 (1964).

In the Introduction to the JANAF Thermochemical Tables (1964) in Section Four dealing with the calculation of entropy appears Table V attributed to K. K. Kelley. In a private communication of June 1960, Kelley presented the table to the publishers of the JANAF Tables. After extensive research, no publication by Kelley was found that explains how he developed the table. The author has published experimental entropy data under the auspices of the U.S. Bureau of Mines, Department of the Interior since the 1390's. The yearly indices to Bureau of Mines publications, which also list outside publications of its employees, give no such publication by K. K. Kelley.

On examination of Table V it can be seen that the entropy values were estimated by assigning a value of zero to the contributions of the oxide anion. Then experimentally determined entropy values were taken into consideration in assigning a value for the cation entropy contribution. This fact is evident from the values given in parentheses. For instance, the entropy values for the Ti^{++} cation, the W^{4+} cation and 2 times the Ti^{5+} cation are equal to the experimentally determined entropy values for TiO, WO_2, and Ti_2O_5 given in the literature. The fact that the values are enclosed in parentheses, usually an indication of lack of confidence in the value, is also a clue since they are probably based on only one experimentally determined entropy value.

The last method investigated was proposed by P. S. Lowell. It follows the same ideas as those of Drozin except an extra volume correction is applied.

TABLE V

KELLEY'S ENTROPY CONSTANTS

ADDITIVE ENTROPY CONSTANTS - K. K. KELLEY

TABLE I. Cations *

Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$
Ag^+	14.8	Cr^{+++}	10.2	Li^+	5.3	Rb^+	15.6	U^{++++}	20.0
Al^{+++}	4.2	Cs^+	(17.5)	Mg^{++}	5.9	Sb^{+++}	(14.7)	U^{++++++}	(23.6)
As^{+++}	(12.8)	Cu^+	11.8	Mn^{++}	12.7	Sb^{++++}	(15.2)	V^{++}	8.2
As^{+++++}	(17.6)	Cu^{++}	10.9	Mn^{+++}	(13.2)	Sb^{+++++}	(15.0)	V^{+++}	10.3
B^{+++}	(6.5)	Fe^{++}	12.6	Mn^{++++}	(12.7)	Si^{++++}	10.2	V^{++++}	(12.3)
Ba^{++}	15.4	Fe^{+++}	9.8	Mo^{++++}	9.4	Sn^{++}	14.0	V^{+++++}	(15.6)
Be^{++}	3.0	Ga^{+++}	(10.2)	Mo^{++++++}	(18.6)	Sn^{++++}	12.9	W^{++++}	(12.1)
Bi^{+++}	(18.1)	Ge^{++++}	(13.2)	Na^+	9.6	Sr^{++}	13.0	W^{++++++}	(18.2)
Ca^{++}	10.0	H^+	3.8	Nb^{++++}	(13.0)	Ta^{+++++}	(17.1)	Y^{+++}	(11.8)
Cd^{++}	13.4	Hf^{++++}	13.9	Nb^{+++++}	(16.4)	Th^{++++}	16.5	Zn^{++}	10.4
Ce^{++}	14.8	Hg^+	16.4	Nd^{+++}	(18.4)	Ti^{++}	(8.3)	Zr^{++++}	11.5
Ce^{+++}	15.9	Hg^{++}	(16.8)	NH_4^+	16.1	Ti^{+++}	9.8		
Co^{++}	11.1	K^+	12.1	Ni^{++}	8.6	Ti^{++++}	12.6		
Cr^{++}	(11.7)	La^{+++}	(15.4)	Pb^{++}	17.5	Tl^+	19.0		

TABLE II. Anions

Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$	Ion	$S^\circ_{298.15}$
AlO_2^-	7.0	ClO_3^-	21.5	HF_2^-	(13.2)	PO_4^{---}	(18.1)	$Si_2O_5^{--}$	(20.7)
BH_4^-	13.4	ClO_4^-	(24.4)	$H_2PO_4^-$	21.8	$P_2O_7^{----}$	(24.5)	Te^{--}	9.1
BO_2^-	7.8	CoO_2^-	8.2	I^-	12.2	ReO_4^-	(28.4)	TiO_3^{--}	11.4
$B_2O_5^{----}$	(14.1)	CrO_4^{--}	23.4	IO_3^-	22.7	S^{--}	3.8	TiO_4^{----}	13.5
$B_4O_7^{--}$	24.2	CrO_2^-	10.0	MnO_4^-	(29.3)	SO_3^{--}	15.0	$Ti_2O_5^{--}$	23.5
Br^-	10.5	$Cr_2O_7^{--}$	(46.2)	NO_2^-	(15.8)	SO_4^{--}	16.4	$Ti_3O_7^{--}$	(37.2)
BrO_3^-	(24.0)	F^-	3.9	NO_3^-	18.9	$S_2O_6^{--}$	(32.0)	VO_3^-	(17.6)
CO_3^{--}	10.5	FeO_2^-	11.7	O^{--}	0.0	Se^{--}	8.5	ZrO_3^{--}	13.7
Cl^-	8.0	$H_2AsO_4^-$	26.6	OH^-	5.1	SiO_3^{--}	9.9		
ClO_2^-	(17.4)	HCO_3^-	(14.6)	PO_3^-	(12.4)	SiO_4^{----}	10.4		

JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan (Aug., 1965).

III. RESULTS

In selecting the best method for estimation of standard entropies the accuracy as well as theoretical basis of the method must be considered. The accuracy of each of the methods under consideration was investigated by comparing the entropy calculated by each method with experimentally obtained entropy values. The root mean square error of the deviations (the RMS error) was determined for each method of estimation. The results are shown in Table VII.

From theoretical considerations it is evident that the entropy contribution for an anion was determined in general by subtracting elemental entropies from known compound entropies. An essentially constant value was obtained for the entropy of an anion in compounds of metals of either the same periodic subgroup (Dr-1) or the same oxidation state (La-2). In order to choose the best method, one must know not only which gives the smallest RMS error but also the best way of grouping the compounds for determining an average entropy contribution for each anion. For instance, the average entropy contribution of the oxide anion could be determined for all metals in the +1 oxidation state, or for all metals in Group la of the periodic table. The RMS error and average anion entropy were determined using both methods of grouping. Since the number of samples in each group was smaller when grouping according to periodic arrangement was employed, additional statistical methods were applied in comparing the accuracy of the two methods of grouping so that sample size would have a minimum effect on the estimation of accuracy.

Tables VIII and IX show that the results as described by the sample variance and the theoretical variance are not appreciably affected by the method of grouping. For the sake of simplicity, it was decided to group the compounds according to metal oxidation state.

Table VII shows that Latimer's method gives the smallest RMS error in 42%, Kelley's in 33%, and Erdős' in 25% of the groups. It is also of interest to note that Kelley's method is most accurate in estimating oxide entropies, and Erdős' in estimating carbonate entropies. Such a result would be expected since Erdős used the carbonates as a basis for estimation and Kelley apparently based part of his estimation on experimentally determined oxide entropies.

In order to be consistent, Latimer's method was chosen for the estimation of all entropies even though the method of Erdős or Kelley might be more accurate in certain cases. Using the method given in Technical Memorandum 004-009-CH2 it may be shown that the uncertainty in entropy, ΔS_u, for an assumed uncertainty in temperature and heat of reaction of 50° C and 50 kcal respectively, will be about 2.5 entropy units at 1000° K and about 25 entropy units at 300° K. Therefore a method such as Latimer's, which has no RMS error greater than 2.9 entropy units should be acceptable. Some of the other methods have individual RMS errors as high as eight entropy units (Drozin and Kelley). A disadvantage to the use of Erdős' method is the fact that it can be applied only to sulfites, sulfates, and carbonates.

The estimation of sulfite entropies is complicated by the fact that there is little experimentally obtained data available. Table X shows Latimer's values for the sulfite anion contribution. Latimer did not give literature references for the experimental data used in estimating sulfite anion entropies, and for the +1 and +3 metal oxidation states the value is considered unreliable. Other TRACOR values were obtained using the same method as Latimer and all the data available in the literature. The values are in agreement with Latimer's (see Figures 1, 2, and 3) therefore it was considered consistent to use Latimer's value when a TRACOR value was unavailable.

TABLE VI

lithium
beryllium
boron
sodium
magnesium
aluminum
silicon
potassium
calcium
scandium
titanium
vanadium
chromium
manganese
iron
cobalt
nickel
copper
zinc
gallium
germanium
arsenic
rubidium
strontium
yttrium
zirconium
niobium
molydenum
ruthenium
rhodium
palladium
silver
cadmium
tin
antimony
cesium
barium
lanthanum
cerium
hafnium
tantalum
rhenium
tungsten
iridium
lead
bismuth
thorium
uranium

TABLE VII

RMS ERROR IN ESTIMATION OF ABSOLUTE ENTROPY

GROUP	RMS ERROR BY METHOD				
	Latimer	Drozin	Erdos	Kelley	Lowell
Metal (I) Oxides	1.441	7.020		1.2964	4.922
Metal (II) Oxides	1.771	2.820		0.988	2.189
Metal (III) Oxides	2.835	4.069		1.266	3.470
Metal (IV) Oxides	1.336	2.018		1.342	1.642
Metal (I) Carbonates	1.557	5.543	0.862	1.630	3.933
Metal (II) Carbonates	2.296	2.526	0.898	1.714	2.296
Metal (I) Sulfates	2.878	7.076	3.985	4.358	5.053
Metal (II) Sulfates	2.816	2.515	1.207	2.215	2.598
Metal (I) Sulfides	0.460	8.058		0.561	6.397
Metal (II)Sulfides	1.823	2.673		1.429	2.203
Metal (III) Sulfides	1.528	3.014		8.969	2.296
Metal (IV) Sulfides	2.047	2.252			3.225
Metal Titanates ($TiO_3^=$)	1.471				
($TiO_4^=$)	1.500				
($Ti_2O_5^=$)	1.850				
Metal (I, II) Ferrites ($Fe_2O_4^=$)	2.100				
(FeO_2^-)	1.760				
Metal (I) Metaaluminates (AlO_2^-)	0.100				
Metal (II) Aluminates ($Al_2O_4^=$)	2.590				
Metal (II) Molybdates ($MoO_4^=$)	0.377				

Table VII
Page 2

	RMS ERROR BY METHOD				
GROUP	Latimer	Drozin	Erdos	Kelley	Lowell
Metal (II) Chromites ($Cr_2O_4^=$)	3.546				
Metal (II) Chromates ($CrO_4^=$)	1.740				
Metal (II) Tungstates ($WO_4^=$)	2.398				
Metal (II) Metavanadates ($V_2O_8^=$)	1.415				

TABLE VIII

ANALYSIS OF ERRORS CAUSED BY GROUPING METHODS BASED ON SMALLEST RMS ERROR

ANION	METHOD OF GROUPING	SMALLEST RMS ERROR	NUMBER IN GROUP N	SAMPLE[1] VARIANCE	THEORETICAL[2] DEVIATION SUM
Oxide	+1 Metals	1.441	5	2.08	13.0
	Group I a Metals	0.987	3	0.975	4.38
	Transition Metals	0.7273	2	0.529	2.116
	Sum, +1 Metals				6.496
Oxide	+2 Metals	1.711	16	2.93	49.92
	Group II a Metals	0.9931	5	0.986	6.16
	Transition Metals	1.952	9	3.81	38.565
	Group IV a Metals	0.1775	2	.032	0.126
	Sum, +2 Metals				44.851
Oxide	+3 Metals	2.835	12	8.04	105.12
	Group V a Metals	0.0001	2	$1.82\text{x}10^{-8}$	$7.28\text{x}10^{-8}$
	Group III a Metals	2.940	3	8.530	38.4
	Transition Metals	2.401	7	5.765	47.18
	Sum, +3 Metals				85.58

TABLE VIII
Page 2

ANION	METHOD OF GROUPING	SMALLEST RMS ERROR	NUMBER IN GROUP N	SAMPLE[1] VARIANCE	THEORETICAL[2] DEVIATION SUM
Oxide	+4 Metals	1.336	15	1.785	28.65
	Group IV a Metals	1.256	4	1.579	8.40
	Transition Metals	1.291	9	1.670	16.89
	Actinides	1.460	2	2.135	8.54
	Sum, +4 Metals				33.83
Sulfate	+1 Metals	2.878	4	8.283	44.07
	Group I a Metals	3.161	3	9.990	44.96
Sulfate	+2 Metals	2.515	12	6.325	82.80
	Group II a Metals	0.788	5	0.620	3.87
	Transition Metals	2.949	6	8.690	62.40
	Sum, +2 Metals				66.27
Carbonate	+2 Metals	2.296	8	5.265	48.20
	Group II a Metals	1.003	3	1.006	4.53
	Transition Metals	2.122	5	4.460	28.40
	Sum, +2 Metals				32.927

[1] Sample Variance = $S^2 = \sum_{i=1}^{N} \frac{(x_i - \bar{x})}{n}$

[2] Theoretical Deviation Sum = $n\sigma^2 = \frac{n^2}{n-1} S^2$

TABLE IX

ANALYSIS OF ERRORS CAUSED BY GROUPING METHOD BASED ON RMS ERROR OF LATIMER'S METHOD

ANION	METHOD OF GROUPINC	RMS ERROR	NUMBER IN GROUP	THEORETICAL[1] DEVIATION SUM	PRECISION[2] CONSTANT
Oxide	+1 Metals	1.441	5	12.978	1.611
	Group Ia Metals	1.445	3	9.396	1.770
	Transition Metals	1.277	2	6.523	1.805
	Sum, +1 Metals			15.919	
Oxide	+2 Metals	1.711	16	49.960	1.766
	Group IIa Metals	1.548	6	17.253	1.697
	Transition Metals	1.952	9	38.580	2.070
	Group IVa Metals	0.178	2	0.126	0.251
	Sum, +2 Metals			55.958	
Oxide	+3 Metals	2.835	12	105.210	2.961
	Group Va Metals	1.118	2	4.999	1.580
	Group IIIa Metals	2.940	3	38.896	3.600
	Transition Metals	2.405	7	47.236	2.597
	Sum, +3 Metals			91.131	

TABLE IX
Page 2

ANION	METHOD OF GROUPING	RMS ERROR	NUMBER IN GROUP	THEORETICAL[1] DEVIATION SUM	PRECISION[2] CONSTANT
Oxide	+4 Metals	1.336	15	28.685	1.383
	Group IVa Metals	1.256	4	8.413	1.448
	Transition Metals	1.291	9	16.875	1.369
	Actinides	1.468	2	8.620	2.076
	Sum, +4 Metals			33.908	
Oxide	+6 Metals	1.670	5	17.430	1.867
Sulfide	+1 Metals	0.460	2	0.846	0.650
Sulfide	+2 Metals	1.823	13	46.803	1.897
Sulfide	+3 Metals	1.528	3	10.506	1.871
Sulfide	+4 Metals	2.047	6	30.169	2.242
Sulfate	+1 Metals	2.878	4	44.065	3.319
	Group 1a Metals	3.161	3	44.963	3.871

TABLE IX
Page 3

ANION	METHOD OF GROUPING	RMS ERROR	NUMBER IN GROUP	THEORETICAL VARIANCE[1]	PRECISION CONSTANT[2]
Sulfate	+2 Metals	2.816	12	103.81	2.941
	Group IIa Metals	1.419	5	12.58	1.587
	Transition Metals	3.410	6	83.72	4.092
	Sum, +2 Metals			96.30	
Carbonate	+1 Metals	1.557	4	12.93	1.796
Carbonate	+2 Metals	2.296	8	48.20	2.451
	Group II-A Metals	2.054	3	18.99	2.516
	Transition Metals	2.355	5	34.66	2.611
	Sum, +2 Metals			53.65	

[1] Theoretical Variance = $n\sigma^2 \quad \frac{n^2}{n-1} (RMS)^2$

[2] Precision Constant = $(\frac{n}{n-1})^{\frac{1}{2}}(RMS)$

TABLE X
AVERAGE ANION ENTROPY CONTRIBUTION ESTIMATED BY THE METHOD OF LATIMER

ANION	METAL OXIDATION STATE	LATIMER'S VALUE	TRACOR VALUE
Oxide	+1	2.4	2.703
Oxide	+2	0.5	0.5714
Oxide	+3	0.5	0.2879
Oxide	+4	1.0	0.5305
Sulfide	+1	8.2	7.94
Sulfide	+2	5.0	5.022
Sulfide	+3	1.3	1.6036
Sulfide	+4	2.5	2.511
Sulfate	+1	22.0	23.69
Sulfate	+2	17.2	16.0
Sulfate	+3	13.7	*
Sulfate	+4	12.0	*
Carbonate	+1	15.2	16.03
Carbonate	+2	11.4	11.39
Carbonate	+3	(8)	*
Sulfite	+1	(19)	*
Sulfite	+2	14.9	*
Sulfite	+3	(11)	*
Metatitanate (TiO_3^{2-})	+1		14.5
Metatitanate (TiO_3^{2-})	+2		12.91
Titanate (TiO_4^{4-})	+2		12.5
Titanate ($Ti_2O_5^{2-}$)	+1,+2		24.65
Ferrite ($Fe_2O_4^{2-}$)	+2		21.67
Ferrite (FeO_2^{-1})	+1		12.83
Metaaluminate (AlO_2^{-1})	+1		9.3

TABLE X
Page 2

ANION	METAL OXIDATION STATE	LATIMER'S VALUE	TRACOR VALUE
Aluminate ($Al_2O_4^{2-}$)	+2		14.88
Molybdate (MoO_4^{2-})	+2		20.27
Chromite ($Cr_2O_4^{2-}$)	+2		19.52
Chromate (CrO_4^{2-})	+2		24.45
Tungstate (WO_4^{2-})	+2		19.26
Metavanadate ($V_2O_6^{2-}$)	+2		32.08

* Lack of experimentally obtained entropies prevented determination of average anion entropy.

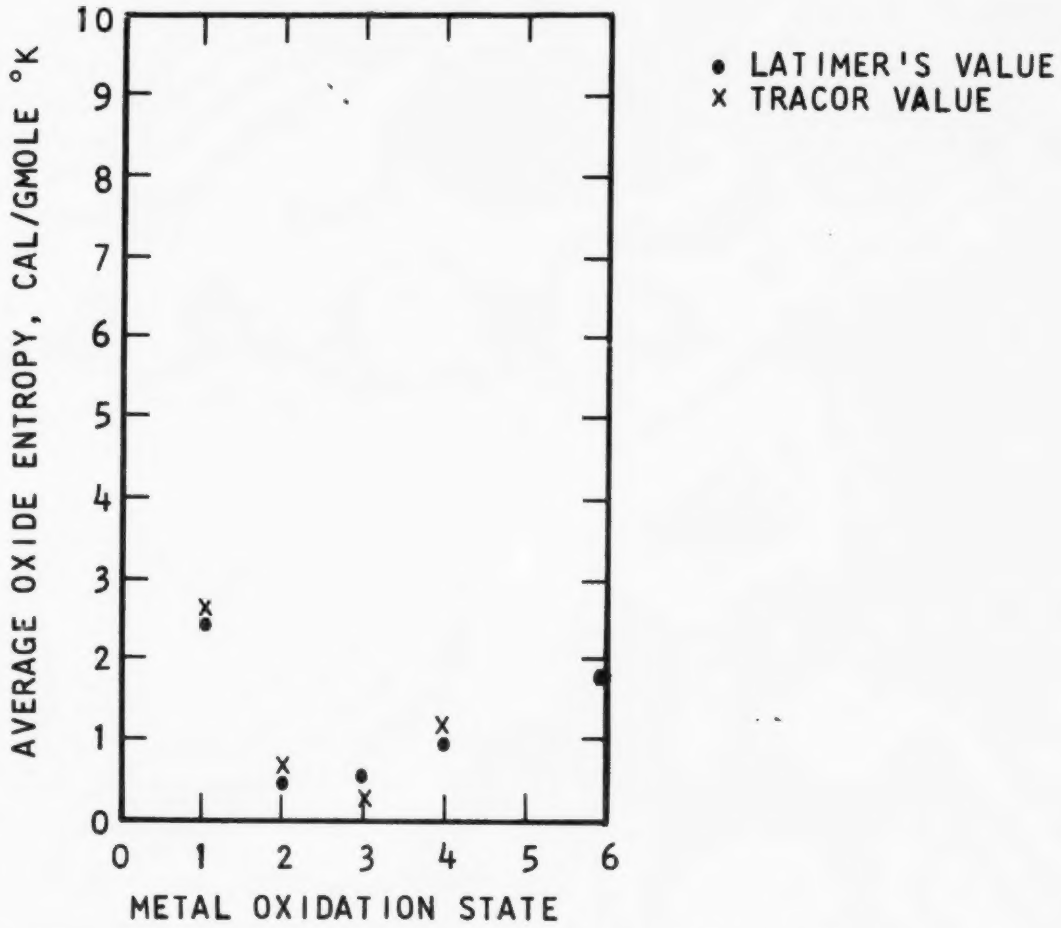


FIG. 1 - AVERAGE OXIDE ENTROPY BY LATIMER'S METHOD VS METAL OXIDATION STATE

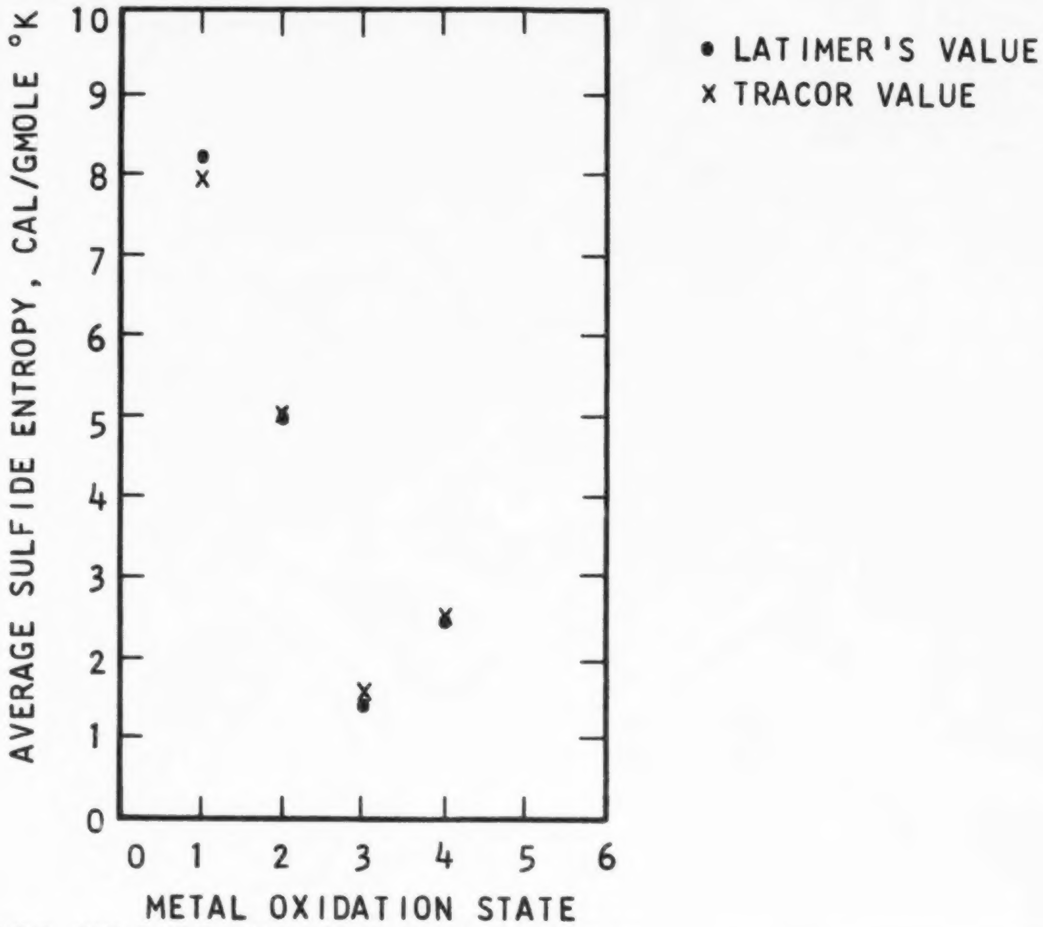


FIG. 2 - AVERAGE SULFIDE ENTROPY BY LATIMER'S METHOD VS METAL OXIDATION STATE

TRACOR DWG. A6-3-782
8/12/66
PARSONS

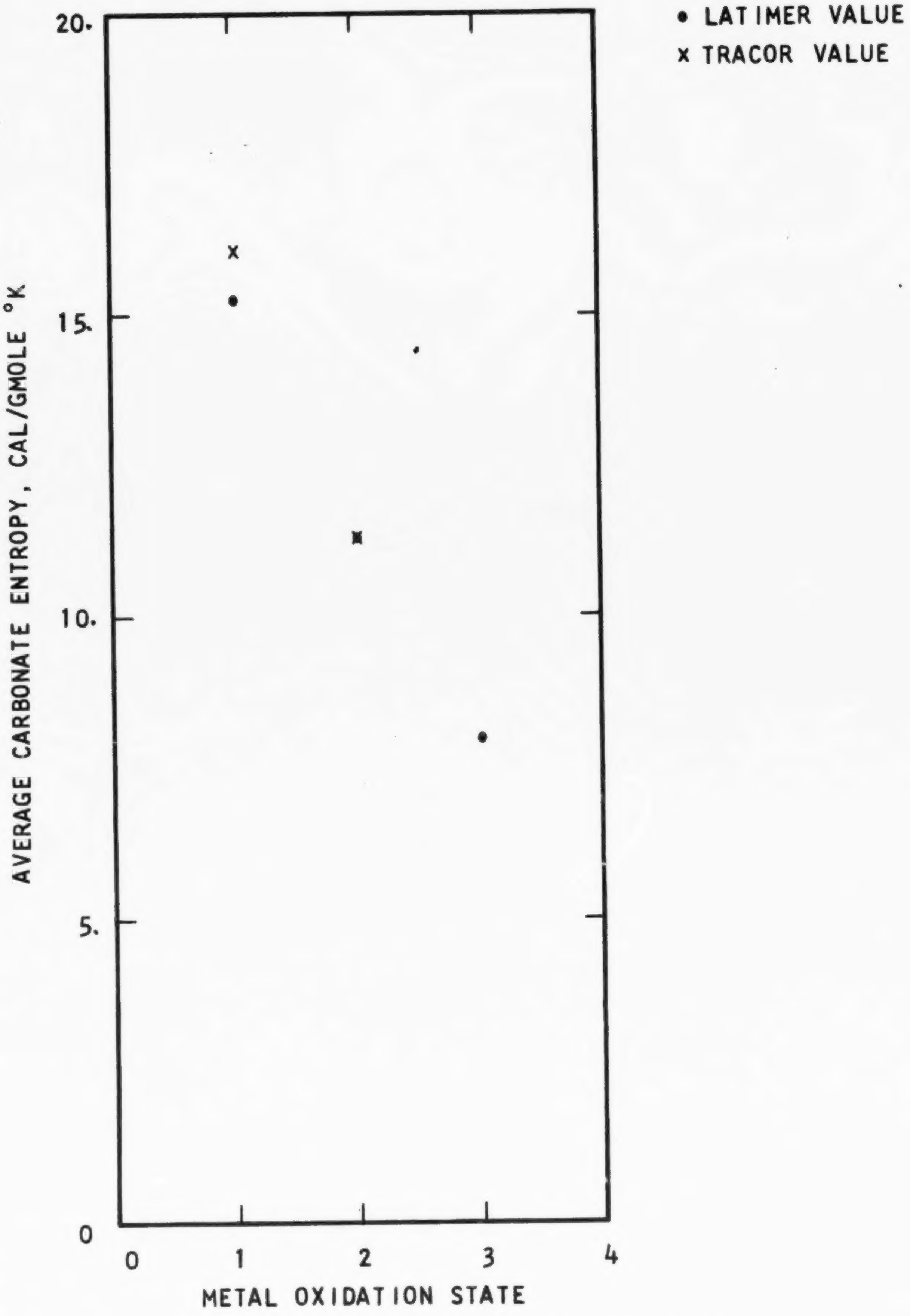


FIG. 3 - AVERAGE CARBONATE ENTROPY BY LATIMER'S METHOD VS METAL OXIDATION STATE

TRACOR DWG.A6-3-780
8/12/66 DP/PARSONS

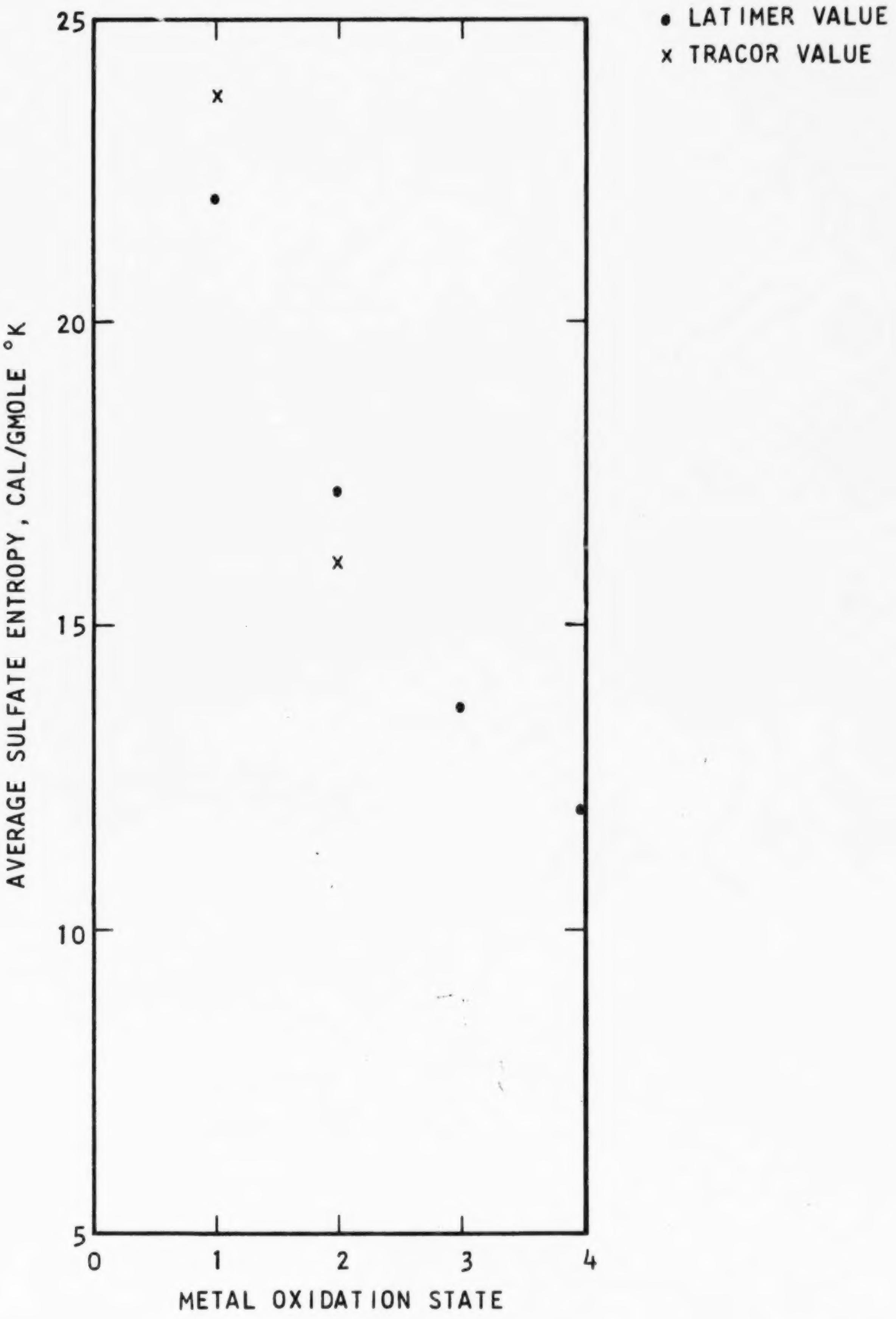


FIG. 4 - AVERAGE SULFATE ENTROPY BY LATIMER'S METHOD VS METAL OXIDATION STATE

TRACOR DWG. A6-3-781
8/12/68 PARSONS

REFERENCES

Da-1 N. Davidson, Statistical Mechanics, Chapter 16, McGraw-Hill (1962).

Dr-1 N. N. Drozin, "Application of Berthelot's Principle to the Calculation of Standard Entropies of Solid Inorganic Compounds," Russian Journal of Physical Chemistry, 38, 1386, (1964).

Er-1 E. Erdös, "Thermodynamic Properties of Sulfites. II. Absolute Entropies, Heat Capacities, and Dissociation Pressures," Collection Czechoslov. Chem. Commun., 27, 2273, (1962).

La-1 W. Latimer, "The Mass Effect in the Entropy of Solids and Gases," Journal of the American Chemical Society, 43, 818, (1921).

La-2 W. Latimer, "Methods of Estimating the Entropies of Solid Compounds," Journal of the American Chemical Society, 73, 1480, (1951).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

24 June 1968 Klaus Schwitzgebel

TECHNICAL MEMORANDUM 004-009-Ch4

SUBJECT: ESTIMATION OF HEAT CAPACITY EQUATIONS FOR SULFATES, CARBONATES AND SULFITES

ESTIMATION OF THE ERROR PROPAGATION

One of the more important thermodynamic properties of a substance is the heat capacity as a function of temperature.

The enthalpy and entropy change of a substance between two temperatures may be calculated if the heat capacity is known. Thus from a knowledge of heat capacity and heat of formation and absolute entropy at 25° C, the enthalpy of formation and absolute entropy may be calculated at any temperature. From this information chemical equilibria may be calculated.

The thermodynamic data listed in various data compilations and in the open literature do not give heat capacity equations for many sulfates, carbonates and sulfites. The oxides and the elements have been investigated more completely. In this memorandum a method of estimating heat capacity equations is outlined. An estimation of the errors and their propagation in the final results is also given.

A) Estimation methods for heat capacities.

The more common methods for estimation of unknown heat capacities are summarized in "Janaf Thermochemical Tables" [1]. There are basically two methods. In the first method some thermodynamic data, like the entropy at the melting temperature, are known and can be used for the estimation. This method cannot be applied in our case, because these quantities are unknown for nearly all sulfites. The second way outlined in Janaf is an extension of Kopps rule:

$$Cp\ (X_{a,}Y_{b,}Z_{c}) \approx a\ Cp\ (X) + b\ Cp\ (Y) + c\ CP(Z)$$

and

$$Cp\ (X_{a,}Y_{b+c}) \approx Cp\ (X_{a,}Y_{b}) + c\ Cp\ (Y) \tag{1}$$

A prerequisite for the application of these formulas is that the compound be composed of solid elements. The heat capacity equations are known for most of the oxides and the elements under investigation. The second method given by Janaf may therefore be modified in the following manners:

a) From the known equations for the oxides and the corresponding salts an average contribution for SO_3, CO_2 and SO_2 lattices can be derived. For instance the unknown heat capacity equation for a sulfate can be estimated as follows:

$$Cp(T)_{MeSO_4} = Cp(T)_{MeO} + \overline{Cp(T)_{SO_3\ \mathrm{lattice}}} \qquad (2)$$

with

$$\overline{Cp(T)_{SO_3\ \mathrm{lattice}}} = \frac{1}{n}\left[\sum_{i=1}^{n} (Cp(T)_{\mathrm{Sulfate}})_i - \sum_{i=1}^{n} (Cp(T)_{\mathrm{Oxide}})_i\right] \qquad (3)$$

b) From the known equations for the elements and the corresponding salts an average contribution for $SO_4^=$, $SO_3^=$ and $CO_3^=$ can be derived. The unknown heat capacity for a sulfate may then be calculated in the following way:

$$Cp(T)_{MeSO_4} = Cp(T)_{Me} + \overline{Cp(T)_{SO_4^=}} \qquad (4)$$

with

$$\overline{Cp(T)_{SO_4^=}} = \frac{1}{n}\left[\sum_{i=1}^{n} (Cp(T)_{MeSO_4})_i - \sum_{i=1}^{n} (Cp(T)_{Me})_i\right] \qquad (5)$$

c) A third way of estimation would be the following:

$$Cp(T)_{Me_i SO_4^=} = Cp(T)_{Me_j SO_4} - Cp(T)_{Me_j} + Cp(T)_{Me_i} \qquad (6)$$

The methods under b and c have the disadvantage that some metals melt at realtively low temperatures in comparison with the oxides used under (a). By trial and error it was found that method (a) gave the best result. A comparison of the various methods is given in Table I.

The heat capacity equation coefficients of the average SO_3, SO_2 and CO_2 lattices are given in Table II. The form of the heat capacity equation is

$$Cp = A + BT - D/T^2 \tag{7}$$

Heat capacities for sulfates, carbonates and sulfites were calculated with equation (2) and similar equations for the carbonates and sulfites. These data are presented in Table II.

$$Cp(T)_{Sulfate} = \overline{Cp(T)_{SO_3\text{-lattice}}} + Cp(T)_{MeO} \tag{8}$$

$$Cp(T)_{Carbonate} = \overline{Cp(T)_{CO_2\text{-lattice}}} + Cp(T)_{MeO} \tag{9}$$

and

$$Cp(T)_{Sulfite} = \overline{Cp(T)_{SO_2\text{-lattice}}} + Cp(T)_{MeO} \tag{10}$$

Table III shows the results. The equations for the oxides used are given with the temperature range in which they are valid.

B) Error Propagation

In Technical Memorandum 004-009-Ch2 the errors in log K and T caused by uncertainties of the heat of formation at 25° C and the standard entropies were estimated. In estimating the errors at higher temperatures the influence of the errors in the $\Delta Cp(T)$- functions were neglected. Here we want to get an idea about the uncertainty caused by the estimation for the Cp(T)-functions as listed in Table III. Neglecting phase transitions, the heat of formation and the entropy of a substance at temperatures higher than 298° K are given by the equations:

$$H_T = H_{298} + \int_{298}^{T} Cp(T)\,dT \tag{11}$$

and

$$S_T = S_{298} + \int_{298}^{T} \frac{Cp(T)}{T}\,dT \tag{12}$$

Let us assume that the exact heat capacity equation for a sulfate is given by

$$Cp(T) = A + BT - \frac{D}{T^2} \qquad (13)$$

We write for the estimated equation

$$Cp'(T) = A' + B'T - \frac{D'}{T^2} \qquad (14)$$

The uncertainties ΔH_u and ΔS_u at the temperature T are obtained by integrating equations 11 and 12.

$$\Delta H_u = \Delta A\ (T-298) + \frac{\Delta B}{2}\ (T^2 - 298^2) + \Delta D\ \left(\frac{1}{T} - \frac{1}{298}\right) \qquad (15)$$

and

$$\Delta S_u = 2.303\ \Delta A\ \log \frac{T}{298} + \Delta B(T-298) + \frac{\Delta D}{2}\ \left(\frac{1}{T^2} - \frac{1}{298^2}\right) \qquad (16)$$

with

$\Delta A = A-A'$; $\Delta B = B-B'$ and $\Delta D = D-D'$;

Let us consider the decomposition reaction:

$$MeSO_4 = MeO + SO_3$$

We assume that only the estimated heat capacity equation of the sulfate is uncertain. Then the uncertainty of log K (Δ logK) for a fixed temperature T is:

$$\Delta \log K = \frac{1}{2.303\ RT} (\Delta H_u - T\Delta S_u) \qquad (17)$$

and the uncertainty in temperature (ΔT_u) for a fixed partial pressure is

$$\Delta T_u = -\frac{T}{\Delta H} (\Delta H_u - T\Delta S_u) \qquad (18)$$

The magnitudes of ΔH_u and ΔS_u are given by equations (15) and (16). ΔH is the heat of reaction at temperature T (for the purposes of estimation ΔH was assumed to be 50 kcal/mole).

We see from equations (11) and (12) that errors in the heat capacity equation will cause errors of the same sign in ΔH_u and ΔS_u. Fortunately in formulas (17) and (18) these errors are subtracted from each other.

Table IV gives the uncertainties for some compounds at various temperatures. The Cp(T)-functions for the listed compounds have been estimated from Cp(T)-functions for the oxides using the equation (2) and data in Table II. Equations (15) and (16) were evaluated, and finally the uncertainties ΔlogK and ΔT were calculated with equations (17) and (18). Comparing the errors as shown in Table IV with the uncertainties involved in the estimation of the heat of formation at 25° C (see Technical Memorandum 004-009-Ch 2) we see that at 1000° K the errors are smaller by the factor .25-.1.

LITERATURE

[1] Janaf Thermochemical Tables, the Dow Chemical Company, Midland, Michigan, August, 1965.

[2] Chemical Abstracts, 58, 7432d.

[3] A. A. Fotiev, Journal of Applied Chemistry USSR, (English translation), 1962, pg. 2307.

[4] A. A. Fotiev: Zh. Prikl. Khim. 35, 2402-2409, 1962, "Thermodynamic analysis of some reactions occuring in the reduction of sodium sulfate with carbon."

TABLE I

COMPARISON OF HEAT CAPACITIES AS ESTIMATED FROM THE EQUATIONS (2), (4) AND (6) WITH THE LITERATURE VALUES

Compound	° K	Cp_{Lit}(cal/mole° K)	Method (a) $Cp_{Lit}-Cp_{Est}$ [cal/mole° K]	Method (b)* $Cp_{Lit}-Cp_{Est}$ [cal/mole° K]	Method (c) $Cp_{Lit}-Cp_{Est}$ [cal/mole° K]	Based on
Na_2SO_4	298	31.23	-0.01	- .33	1.02	K_2SO_4
$CaSO_4$	298	23.81	-0.44	- .55	.64	$MgSO_4$
	700	33.51	-0.39	-1.12	1.65	
	1000	40.56	+0.77	- .62	2.00	
$MnSO_4$	298	23.97	-0.66	- .10	-8.89	$NiSO_4$
	700	34.05	+0.15	-1.90	-2.99	
	1000	37.46	-2.50	-6.17	-2.71	
$CuSO_4$	298	23.89	-0.75	- .06	.84	$ZnSO_4$
	700	30.82	-3.43	-2.60	- .22	
$1/3Al_2(SO_4)_3$	298	20.63	+0.43	-4.53	- .45	$ZnSO_4$
	700	30.85	-0.05	-2.9	1.58	
	1000	33.27	-3.73	-7.42	-2.10	
$PbSO_4$	298	24.90	-0.83	.49	.55	$BaSO_4$
	700	33.50	-1.52	- .71	1.80	
	1000	42.38	0.77	2.05	10.07	
		RMS =	1.58	3.05	3.80	

$$* \; \overline{Cp(T)_{SO_4^=}} = 15.175 + 17.429\cdot10^{-3}\,T - \frac{2.029}{T^2}\cdot10^5$$

Calculated from equations for Na, Ca, Cu, Mn, Pb and Al

TABLE II

HEAT CAPACITY COEFFICIENTS FOR SO_3, SO_2 AND CO_2 LATTICES

Lattice	A cal/(gmole° C)	$B \cdot 10^3$ cal/(gmole° C^2)	$D \cdot 10^{-5}$ (cal° C)/gmole
SO_3 *	9.30	17.74	0.58
CO_2 **	5.64	16.71	1.39
SO_2 ***	6.91	15.10	----

* Based upon sulfates and oxides of Ag, Al, Ba, Be, Ca, Cd, Cu, Mg, Mn, Na, Pb, Sr, and Zn.

** Based upon carbonates and oxides of Ag, Ba, Ca, Fe, Mg, Mn, Na, Pb, Sr. and Zn.

*** Based upon Na_2SO_3 and Na_2O only.

In Chemical Abstracts [2] the wrong B value ($B=205.0 \times 10^{-3}$) for Na_2SO_3 was evident. The English translation [3] of the original article [4] gives the more reasonable equation $Cp = 22.6+20.5 \times 10^{-3}\,T$ [cal/mole° K].

TABLE III

ESTIMATED HEAT CAPACITY EQUATIONS FOR SULFATES, CARBONATES AND SULFITES

and sulfites.

Heat capacity equation:

$$Cp = A + BT - \frac{D}{T^2} \; [\text{cal/mole } ^\circ K]$$

Compound	A	$B \cdot 10^3$	$D \cdot 10^{-5}$	Temperature Range for Oxide Equation °C
Ag_2O	13.25	7.04	---	25-700
Ag_2SO_3	20.16	22.14	---	
Al_2O_3	26.41	4.34	7.92	25-700
$Al_2(SO_3)_3$	47.14	49.64	7.92	
$Al_2(CO_3)_3$	43.33	54.47	12.09	
BaO	12.73	1.04	1.98	25-700
$BaSO_3$	19.64	16.14	1.98	
BeO	8.45	4.00	3.17	25-700
$BeSO_3$	15.36	19.10	3.17	
$BeCO_3$	14.09	20.71	4.56	
Bi_2O_3	24.73	8.00	---	25-500
$Bi_2(SO_3)_3$	45.46	53.30	---	
$Bi_2(CO_3)_3$	41.65	58.13	4.17	
$Bi_2(SO_4)_3$	52.63	61.22	1.74	

TABLE III
Page 2

Compound	A	$B \cdot 10^3$	$D \cdot 10^{-5}$	Temperature Range for Oxide Equation °C
CaO	11.86	1.08	1.66	25-600
$CaSO_3$	18.77	16.18	1.66	
CdO	9.65	2.08	---	25-700
$CdSO_3$	16.56	17.18	---	
$CdCO_3$	15.29	18.79	1.39	
CeO_2	15.01	2.51	---	25-1700
$Ce(SO_3)_2$	28.83	32.71	---	
$Ce(CO_3)_2$	26.29	35.93	2.78	
$Ce(SO_4)_2$	33.61	37.99	1.16	
CoO	11.53	2.04	-0.40	25-1200
$CoSO_3$	18.44	17.14	-0.40	
$CoCO_3$	17.17	18.75	.99	
Cr_2O_3	28.53	2.20	3.74	25-1200
$Cr_2(SO_3)_3$	49.26	47.50	3.74	
$Cr_2(CO_3)_3$	45.45	52.33	7.91	
$Cr_2(SO_4)_3$	56.43	55.42	5.48	
CuO	9.27	4.80	---	25-700
$CuSO_3$	16.18	19.90	---	
$CuCO_3$	14.91	21.51	1.39	
Cu_2O	14.89	5.70	---	25-700
Cu_2SO_3	21.80	20.80	---	
Cu_2CO_3	20.53	23.44	1.39	
Cu_2SO_4	24.19	23.44	0.58	

TABLE III

Page 3

Compound	A	$B\cdot10^3$	$D\cdot10^{-5}$	Temperature Range for Oxide Equation °C
FeO	11.66	2.00	.76	25-1200
$FeSO_3$	18.57	17.10	---	
$FeSO_4$	20.96	19.74	1.34	
Fe_2O_3	23.48	18.59	3.55	25-677
$Fe_2(SO_3)_3$	44.21	63.89	3.55	
$Fe_2(CO_3)_3$	40.40	68.72	7.72	
$Fe_2(SO_4)_3$	51.38	71.81	5.29	
Ga_2O_3	11.77	25.18	---	25-600
$Ga_2(SO_3)_3$	32.50	70.48	---	
$Ga_2(CO_3)_3$	28.69	75.31	4.17	
$Ga_2(SO_4)_3$	39.67	78.40	1.74	
GeO_2	11.20	7.17	---	25-700
$Ge(SO_3)_2$	25.02	37.37	---	
$Ge(CO_3)_2$	22.48	40.59	2.78	
$Ge(SO_4)_2$	29.80	42.65	1.16	
HfO_2	17.38	2.08	3.48	25-1200
$Hf(SO_3)_2$	31.20	32.28	3.48	
$Hf(CO_3)_2$	28.66	35.50	6.26	
$Hf(SO_4)_2$	35.98	37.56	4.64	
IrO_2	9.17	15.20	---	25-700
$Ir(SO_3)_2$	22.99	45.40	---	
$Ir(CO_3)_2$	20.45	48.62	2.78	
$Ir(SO_4)_2$	27.77	50.68	1.16	

TABLE III
Page 4

Compound	A	$B \cdot 10^3$	$D \cdot 10^{-5}$	Temperature Range for Oxide Equation °C
K_2O	17.91	9.32	0.40	25-1200
K_2SO_3	24.82	24.42	.40	
K_2CO_3	23.55	26.03	1.79	
La_2O_3	28.86	3.07	3.27	25-700
$La_2(SO_3)_3$	49.59	48.37	3.27	
$La_2(CO_3)_3$	45.78	53.20	7.44	
$La_2(SO_4)_3$	56.76	56.29	5.01	
Li_2O	14.93	6.08	3.38	25-700
Li_2SO_3	21.84	21.18	3.38	
Li_2CO_3	20.57	22.79	4.77	
Li_2SO_4	24.23	23.82	3.96	
MgO	10.18	1.74	1.48	25-700
$MgSO_3$	17.09	16.84	1.48	
MnO	11.10	1.94	0.88	25-1200
$MnSO_3$	18.01	17.04	0.88	
MnO_2	16.59	2.44	3.88	25-500
$Mn(SO_3)_2$	30.41	32.64	3.88	
$Mn(CO_3)_2$	27.87	35.86	6.66	
$Mn(SO_4)_2$	35.19	37.92	5.04	
Mn_2O_3	24.73	8.38	3.23	25-700
$Mn_2(SO_3)_3$	45.46	53.68	3.23	
$Mn_2(CO_3)_3$	41.65	58.51	7.40	
$Mn_2(SO_4)_3$	52.63	61.60	4.97	

TABLE III
Page 5

Compound	A	$B\cdot10^{3}$	$D\cdot10^{-5}$	Temperature Range for Oxide Equation °C
MoO_3	20.06	5.90	3.68	25-700
$Mo(SO_3)_3$	40.79	51.20	3.68	
$Mo(CO_3)_3$	36.98	56.03	7.85	
$Mo(SO_4)_3$	47.96	59.12	5.42	
Nb_2O_5	36.22	5.54	4.88	25-1200
$Nb_2(SO_3)_5$	70.77	81.04	4.88	
$Nb_2(CO_3)_5$	64.42	89.04	11.83	
$Nb_2(SO_4)_5$	82.72	94.24	7.78	
$NiSO_4$ *	30.08	9.92	---	25-700 (for the sulfate)
$NiSO_3$	27.69	7.28	-.58	
$NiCO_3$	26.42	8.89	.81	
PbO	10.60	4.00	---	25-600
$PbSO_3$	17.51	19.10	---	
PbO_2	12.70	7.80	---	25-700
$Pb(SO_3)_2$	26.52	38.00	---	
$Pb(CO_3)_2$	23.98	41.22	2.78	
$Pb(SO_4)_2$	31.30	43.28	1.16	
PdO	3.30	14.19	---	25-500
$PdSO_3$	10.21	29.29	---	
$PdCO_3$	8.94	30.90	1.39	
$PdSO_4$	12.60	31.93	.58	
RhO	9.84	5.53	---	25-700
$RhSO_3$	16.75	20.63	---	
$RhCO_3$	15.48	22.24	1.39	
$RhSO_4$	19.40	23.27	.58	

Table III
Page 6

Compound	A	$B \cdot 10^3$	$D \cdot 10^{-5}$	Temperature Range for Oxide Equation °C
Sb_2O_3 **	9.55	8.54	---	25-900° C
$Sb_2(SO_3)_3$	30.28	53.84	---	
$Sb_2(CO_3)_3$	26.47	58.67	4.17	
$Sb_2(SO_4)_3$	37.45	61.76	1.74	
SnO	9.55	3.50	---	25-700
$SnSO_3$	16.46	18.60	---	
$SnCO_3$	15.19	20.21	1.39	
$SnSO_4$	18.85	21.24	.58	
SnO_2	17.66	2.40	5.16	25-1200
$Sn(SO_3)_2$	31.48	32.60	5.16	
$Sn(CO_3)_2$	28.94	35.82	7.94	
$Sn(SO_4)_2$	36.26	37.88	6.32	
SrO	12.33	1.12	1.81	25-700
$SrSO_3$	19.24	16.22	1.81	
Ta_2O_5	36.98	6.56	5.95	25-1200
$Ta_2(SO_3)_5$	71.53	82.06	5.95	
$Ta_2(CO_3)_5$	65.18	90.11	12.90	
$Ta_2(SO_4)_5$	83.48	95.26	8.85	
ThO_2	15.83	2.88	1.60	25-1200
$Th(SO_3)_2$	29.65	33.08	1.60	
$Th(CO_3)_2$	27.11	36.30	4.38	

Compound	A	$B \cdot 10^3$	$D \cdot 10^{-5}$	Temperature Range for Oxide Equation °C
TiO	10.56	3.60	1.86	25-1000
$TiSO_3$	17.47	18.70	1.86	
$TiCO_3$	16.20	20.31	3.25	
$TiSO_4$	19.86	21.34	2.44	
TiO_2	17.13	.98	3.50	25-1200
$Ti(SO_3)_2$	30.95	31.18	3.50	
$Ti(CO_3)_2$	28.41	34.40	6.28	
$Ti(SO_4)_2$	35.73	36.46	4.66	
Ti_2O_3 ***	35.24	.75	10.96	25-1200
$Ti_2(SO_3)_3$	55.97	46.05	10.96	
$Ti_2(CO_3)_3$	52.16	50.88	15.13	
$Ti_2(SO_4)_3$	63.14	53.97	12.70	
UO_2	19.19	1.62	3.96	25-1200
$U(SO_3)_2$	33.01	31.82	3.96	
$U(CO_3)_2$	30.47	35.04	6.74	
$U(SO_4)_2$	37.79	37.10	5.12	
UO_3	22.08	2.54	2.97	25-600
$U(SO_3)_3$	42.81	47.84	2.97	
$U(CO_3)_3$	39.00	52.67	7.14	
$U(SO_4)_3$	49.98	55.76	4.71	
VO	11.31	3.22	1.26	25-1200
VSO_3	18.22	18.32	1.26	
VCO_3	16.95	19.93	2.65	
VSO_4	20.61	20.96	1.84	

Compound	A	$B\cdot10^3$	$D\cdot10^{-5}$	Temperature Range for Oxide Equation °C
V_2O_3	29.34	4.76	5.42	25-1200
$V_2(SO_3)_3$	50.07	50.06	5.42	
$V_2(CO_3)_3$	46.26	54.89	9.59	
$V_2(SO_4)_3$	57.24	57.98	7.16	
WO_2	17.83	1.89	3.34	25-1200
$W(SO_3)_2$	31.65	32.09	3.34	
$W(CO_3)_2$	29.11	35.31	6.12	
$W(SO_4)_2$	36.43	37.37	4.50	
WO_3	22.30	1.93	4.80	25-1200
$W(SO_3)_3$	43.03	47.23	4.80	
$W(CO_3)_3$	39.22	52.06	8.97	
$W(SO_4)_3$	50.20	55.15	6.54	
ZnO	11.70	12.18	2.18	25-1200
$ZnSO_3$	18.61	27.28	2.18	

* NiO has at 250°C a phase transition with a change in Cp of about 3 cal/mole°K.
The values for the sulfite and the carbonate have been therefore estimated from the equation for the sulfate, which is given in Landolt-Boernstein, in the following way

$$Cp_{NiSO_3} = Cp_{NiSO_4} - Cp_{SO_3\,\text{lattice}} + Cp_{SO_2\,\text{lattice}}$$

and

$$Cp_{NiCO_3} = Cp_{NiSO_4} - Cp_{SO_3\,\text{lattice}} + Cp_{CO_2\,\text{lattice}}$$

** Landolt Boernstein gives for Sb_4O_6 the heat capacity equation

$$Cp = 79.9 + 71.5 \cdot 10^{-3} \cdot T \quad \text{joules/mole}°K$$

$$= 19.09 + 17.08 \cdot 10^{-3} \cdot T \quad \text{cal/mole}°K$$

It was assumed that

$$Cp_{Sb_2O_3} = \frac{1}{2} Cp_{Sb_4O_6}$$

$$= 9.55 + 8.54 \cdot 10^{-3} \cdot T \text{ cal/mole}°K$$

*** For Ti_2O_3 the α - β - phase transition was neglected. From the values listed in Janaf [1] an overall heat capacity equation was calculated.
The equation for the oxide is therefore different from that listed in the data file.

TABLE IV

ERRORS IN LOG K AND TEMPERATURE ***

	ΔLog K			ΔT[°K]		
	500° K	700° K	1000° K	500° K	700° K	1000° K
Na_2SO_4	0.04	*	*	-0.9	*	*
$CaSO_4$	-0.02	-0.04	-0.06	0.40	1.7	5.6
$MnSO_4$	0.01	0.04	-0.07	-0.25	-1.9	- 6.4
$CuSO_4$	-0.03	-0.10	**	0.75	4.5	**
$1/3Al_2(SO_4)_3$	-0.03	-0.09	0.13	-0.80	-3.88	-11.4
$PbSO_4$	-0.05	-0.12	-0.21	1.05	5.53	19.6

* The literature heat capacity equation for Na_2SO_4 on which the estimation is based is valid only in the temperature range 25...259° C

** The literature heat capacity equation of $CuSO_4$ is valid only in the range 25-600° C

*** The heat of reaction was assumed to be 50 kcal/mole

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

28 October 1968

T. B. Parsons
P. S. Lowell

TECHNICAL MEMORANDUM 004-009-Ch9

ESTIMATION OF HEAT CAPACITY OF MIXED METAL OXIDES

In order to estimate the heat capacity of mixed metal oxides, it was assumed that the heat capacity of the mixed oxide was the sum of the heat capacities of the constituent oxides. For instance, the heat capacity of $ZnCr_2O_4$ was assumed equal to the sum of the heat capacities of ZnO and Cr_2O_3. The validity of such an assumption is illustrated in Figure 1.

The estimation of mixed oxide heat capacities is therefore only a matter of adding the coefficients of the constituent oxide heat capacity equations. There may be, however, more than one set of A, B, and D values for a particular oxide. Consider, for example, the case of Fe_2O_3 which has phase transitions at 677 and 767° C. There are three sets of heat capacity coefficients for Fe_2O_3, each set being valid over a particular temperature range.

The fact that Fe_2O_3 has transitions at 677 and 767° C is no guarantee that $CaFe_2O_4$ or $ZnFe_2O_4$ will also have a phase transition at those temperatures. Therefore, there is no reason to describe the heat capacity of $CaFe_2O_4$ with three sets of coefficients, each set being valid over a particular temperature range. The best description of the mixed oxide heat capacity would be one set of A, B, and D values that describe the heat capacity over the whole temperature range of validity.

The temperature range of validity will be that range in which data exist for both of the constituent oxides. The heat capacity equation of each of the constituent oxides is valid over a particular temperature range. For instance, one metal oxide may have valid heat capacity equations from 298 to 700° K, while the second oxide may have valid heat capacity equations from 450 to 1,000° K. The estimated heat capacity equation of the resulting mixed metal oxide would be based on data from 450 to 700° K, the temperature range in which data exist for both of the constituent oxides. This would be considered its valid range.

The following equations describe the method used to compute one set of coefficients that describe the heat capacity equation of a mixed oxide over the total temperature range of validity. The heat capacities of the component single metal oxides are given in Equations 1 and 2.

$$Cp_1 = a_1 + b_1 T - d_1/T^2 \qquad (1)$$

$$Cp_2 = a_2 + b_2 T - d_2/T^2 \qquad (2)$$

The heat capacity of the mixed oxide is given by Equation 3.

$$Cp_3 = a_3 + b_3 T - d_3/T^2 \qquad (3)$$

Consider the reaction:

$$\alpha_1 \text{ Metal Oxide}_1 + \alpha_2 \text{ Metal Oxide}_2 \rightarrow \text{Mixed Metal Oxide}_3$$

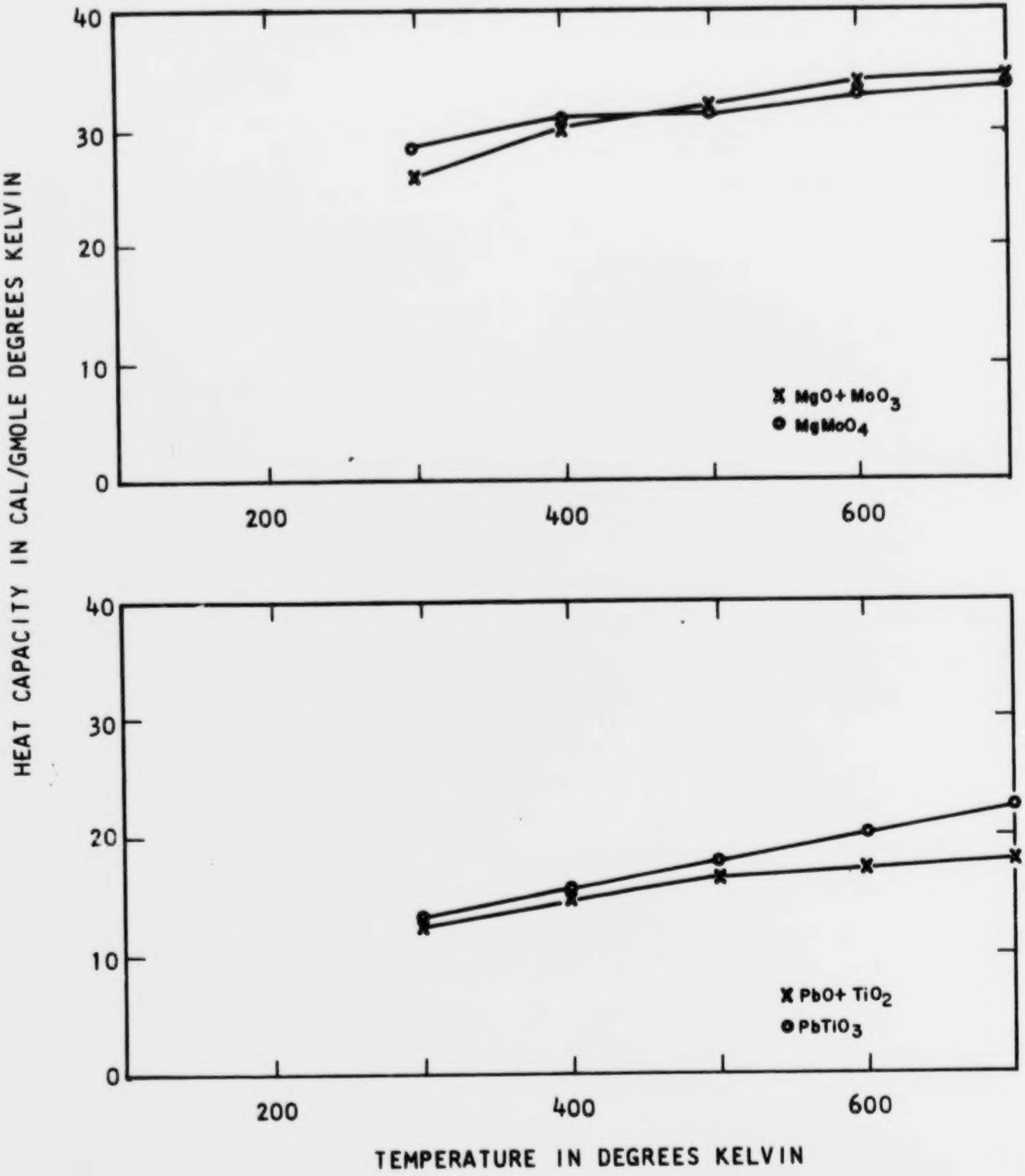


FIG. 1 - COMPARISON OF ESTIMATED AND ACCEPTED VALUES FOR HEAT CAPACITIES OF MIXED METAL OXIDES

TRACOR DWG. A6-164-1
10/21/68
D.P./PARSONS

The heat capacity equation coefficients for the mixed metal oxide will be described by Equations 4a, 4b, and 4c.

$$a_3 = \alpha_1 a_1 + \alpha_2 a_2 \tag{4a}$$

$$b_3 = \alpha_1 b_1 + \alpha_2 b_2 \tag{4b}$$

$$d_3 = \alpha_1 d_1 + a_2 d_2 \tag{4c}$$

If either of the single metal oxides has more than one set of heat capacity coefficients, there will be more than one resulting set of coefficients for the mixed oxide, each set being valid for a particular temperature interval. If there are I temperature intervals, then the "true" heat capacity coefficients for each interval can be described by Equations 5a, 5b, and 5c.

$$A_i = \alpha_1 a_{1i} + \alpha_2 a_{2i} \tag{5a}$$

$$B_i = \alpha_1 b_{1i} + \alpha_2 b_{2i} \tag{5b}$$

$$D_i = \alpha_1 d_{1i} + \alpha_2 d_{2i} \tag{5c}$$

Since A_i, B_i, and D_i, which describe the "true" heat capacity, are different for each temperature range, the heat capacity as described by a single set of coefficients a_3, b_3, and d_3 will not be the "true" heat capacity at all temperatures. Let ΔCp be the error involved in describing the "true" heat capacity at temperature T with the coefficients a_3, b_3, and d_3 (Equations 6a and 6b).

$$\Delta Cp = \alpha_1 Cp_{1i} + \alpha_2 Cp_{2i} - Cp_3 \tag{6a}$$

$$\Delta Cp = (A_i - a_3) + (B_i - b_3)T - (D_i - d_3)/T^2 \qquad (6b)$$

Equation 7 describes the squared error, Δ^2, for the whole temperature range of validity.

$$\Delta^2 = \sum_{i=1}^{I} \int_{T_{i-1}}^{T_i} [(A_i - a_3) + (B_i - b_3)T - (D_i - d_3)/T^2]^2 dT \qquad (7)$$

For the squared error, Δ^2, to be a minimum, Equations 8, 9, and 10 must be true.

$$\frac{\partial \Delta^2}{\partial a_3} = 0 \qquad (8)$$

$$\frac{\partial \Delta^2}{\partial b_3} = 0 \qquad (9)$$

$$\frac{\partial \Delta^2}{\partial d_3} = 0 \qquad (10)$$

Using Equation 8 and performing the indicated operations on Equation 7 gives Equation 11.

$$a_3 (T_I - T_o) + b_3 \frac{(T_I^2 - T_o^2)}{2} + d_3 \left(\frac{1}{T_I} - \frac{1}{T_o}\right)$$

$$= \sum_{i=1}^{I} A_i (T_i - T_{i-1}) + \sum_{i=1}^{I} B_i \frac{(T_i^2 - T_{i-1}^2)}{2} + \sum_{i=1}^{I} D_i \left(\frac{1}{T_i} - \frac{1}{T_{i-1}}\right) \qquad (11)$$

From Equation 9 we get Equation 12.

$$a_3\frac{(T_I^2-T_o^2)}{2} + b_3\frac{(T_I^3-T_o^3)}{3} - d_3\ln\left(\frac{T_I}{T_o}\right)$$

$$= \sum_{i=1}^{I} A_i\frac{(T_i^2-T_{i-1}^2)}{2} + \sum_{i=1}^{I} B_i\frac{(T_i^3-T_{i-1}^3)}{3} - \sum_{i=1}^{I} D_i\ln\left(\frac{T_i}{T_{i-1}}\right) \qquad (12)$$

The derivative indicated in Equation 10 is shown in Equation 13.

$$a_3\left(\frac{1}{T_I} - \frac{1}{T_o}\right) - b_3\ln\left(\frac{T_I}{T_o}\right) - d_3\left(\frac{1}{3T_I^3} - \frac{1}{3T_o^3}\right)$$

$$= \sum_{i=1}^{I} A_i\left(\frac{1}{T_i} - \frac{1}{T_{i-1}}\right) - \sum_{i=1}^{I} B_i\ln\left(\frac{T_i}{T_{i-1}}\right) - \sum_{i=1}^{I} D_i\left(\frac{1}{3T_i^3} - \frac{1}{3T_{i-1}^3}\right) \qquad (13)$$

From Equations 11, 12, and 13 the values of the coefficients a_3, b_3, and d_3 can be calculated. The RMS error for each estimated equation is calculated from Equation 14.

$$\text{RMS} = \left[\frac{\Delta^2}{T_I-T_o}\right]^{\frac{1}{2}} \qquad (14)$$

Substituting Equation 7 for Δ^2, we get Equation 15.

$$\mathrm{RMS} = \left[\frac{1}{T - T_0} \sum_{i=1}^{I} \int_{T_{i-1}}^{T_i} [A_i - a_3) + (B_i - b_3)T - (D_i - d_3)/T^2]^2 \, dT \right]^{\frac{1}{2}} \quad (15)$$

The RMS error for the whole correlation is found by computing the root mean square of the RMS error for each estimated heat capacity equation.

Examples of the results of the estimation are given in the following pages of computer output. The RMS error was 0.95 Cal/gmole° K. The estimated heat capacity values for mixed metal oxides were added to the TRACOR data base with a reference to this memorandum.

P J Lowell
J. Parsons

```
              HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                        HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                    REACTION:  1.0 BAO     +  1.0 FE203   --->  1.0 (BA    )1(FE204)1


         OXIDE                  A              B              D           TEMPERATURE RANGE
                                                                          DEGREES CENTIGRADE

CATION   BAO               1.2733+01      1.0392-03      1.9829+05      2.5000+01 TO  7.0000+02
ANION    FE203             2.3479+01      1.8591-02      3.5477+05      2.5000+01 TO  6.7700+02
                           3.5978+01      0.0000         0.0000         6.7700+02 TO  7.6700+02
                           3.1702+01      1.7583-03      0.0000         7.6700+02 TO  1.2000+03

         ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                        HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                    REACTION:  1.0 BAO     +  1.0 FE203   --->  1.0 (BA    )1(FE204)1

                  A              B              D           TEMPERATURE  RANGE       RMS  ERROR
                                                            DEGREES CENTIGRADE

             3.6212+01      1.9630-02      5.5305+05      2.5000+01 TO  6.7700+02     3.6597-01
             4.8712+01      1.0392-03      1.9829+05      6.7700+02 TO  7.0000+02     4.0625+00


MIXED METAL OXIDE          A              B              D              TEMPERATURE  RANGE    RMS  ERROR
                                                                        DEGREES CENTIGRADE

(BA    )1(FE204)1      3.9190+01      1.5794-02      7.5875+05      2.5000+01 TO  7.0000+02  8.3169-01
```

```
                HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                          HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                       REACTION:  1.0 BAO     + 1.0 CR203    --->  1.0 (BA    )1(CR204)1

          OXIDE                A             B               D            TEMPERATURE RANGE
                                                                          DEGREES CENTIGRADE

CATION    BAO              1.2733+01     1.0392-03       1.9829+05      2.5000+01 TO  7.0000+02
ANION     CR203            2.8525+01     2.1979-03       3.7388+05      2.5000+01 TO  1.2000+03
      ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                          HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                       REACTION:  1.0 BAO     + 1.0 CR203    --->  1.0 (BA    )1(CR204)1

                    A            B             D            TEMPERATURE  RANGE        RMS  ERROR
                                                            DEGREES CENTIGRADE

                4.1258+01    3.2371-03     5.7217+05     2.5000+01 TO  7.0000+02      1.0034-04


MIXED METAL OXIDE        A             B              D            TEMPERATURE  RANGE     RMS  ERROR
                                                                   DEGREES CENTIGRADE

(BA   )1(CR204)1     4.1258+01     3.2371-03      5.7214+05     2.5000+01 TO  7.0000+02   1.0034-04
```

```
              HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                         HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                 REACTION:  1.0 BAO      + 1.0 V205    ---> 1.0 (BA   ))(V206 ))

          OXIDE                 A             B             D            TEMPERATURE RANGE
                                                                         DEGREES CENTIGRADE

CATION    BAO              1.2733+01     1.0392-03     1.9829+05     2.5000+01 TO  7.0000+02
ANION     V205             4.6514+01     3.8988-03     1.3214+06     2.5000+01 TO  6.7000+02
                           4.5582+01     0.0000        0.0000        6.7000+02 TO  1.2000+03

        ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                         HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                 REACTION:  1.0 BAO      + 1.0 V205    ---> 1.0 (BA   ))(V206 ))

               A              B             D          TEMPERATURE  RANGE        RMS  ERROR
                                                       DEGREES CENTIGRADE

          5.9247+01      4.9381-03     1.5196+06     2.5000+01 TO  6.7000+02      2.9644-01
          5.8315+01      1.0392-03     1.9829+05     6.7000+02 TO  7.0000+02      2.4603+00


MIXED METAL OXIDE          A             B             D          TEMPERATURE  RANGE     RMS  ERROR
                                                                  DEGREES CENTIGRADE

(BA   ))(V206 ))       6.1705+01     1.7643-03     1.6890+06     2.5000+01 TO  7.0000+02   5.9413-01
```

```
              HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                        HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                  REACTION:  1.0 BAO     +  1.0 TIO2    --->  1.0 (BA    ))(TIO3 ))

        OXIDE                 A             B              D            TEMPERATURE RANGE
                                                                        DEGREES CENTIGRADE

CATION  BAO                1.2733+01     1.0392-03      1.9829+05     2.5000+01 TO  7.0000+02
ANION   TIO2               1.7132+01     9.7949-04      3.4975+05     2.5000+01 TO  1.2000+03
      ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                        HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                  REACTION:  1.0 BAO     +  1.0 TIO2    --->  1.0 (BA    ))(TIO3 ))

               A              B              D           TEMPERATURE  RANGE       RMS  ERROR
                                                         DEGREES CENTIGRADE

           2.9865+01      2.0187-03      5.4804+05     2.5000+01 TO  7.0000+02     6.1379-05


MIXED METAL OXIDE         A              B              D            TEMPERATURE  RANGE    RMS  ERROR
                                                                     DEGREES CENTIGRADE

(BA    ))(TIO3 ))     2.9865+01      2.0187-03      5.4802+05     2.5000+01 TO  7.0000+02   6.1379-05
```

```
                 HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                              HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                      REACTION:  1.0 BAO     +  1.0 WO3     --->  1.0 (BA    ))(WO4  ))

         OXIDE                  A               B               D             TEMPERATURE RANGE
                                                                              DEGREES CENTIGRADE

CATION   BAO               1.2733+01       1.0392-03       1.9829+05       2.5000+01 TO  7.0000+02
ANION    WO3               2.2297+01       1.9296-03       4.7967+05       2.5000+01 TO  1.2000+03

        ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                              HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                      REACTION:  1.0 BAO     +  1.0 WO3     --->  1.0 (BA    ))(WO4  ))


                A               B               D             TEMPERATURE  RANGE          RMS  ERROR
                                                              DEGREES CENTIGRADE

            3.5030+01       2.9688-03       6.7796+05       2.5000+01 TO  7.0000+02       7.9862-05



MIXED METAL OXIDE           A               B               D             TEMPERATURE  RANGE     RMS  ERROR
                                                                          DEGREES CENTIGRADE

(BA    ))(WO4  ))       3.5030+01       2.9688-03       6.7794+05       2.5000+01 TO  7.0000+02   7.9862-05
```

```
                 HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                           HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                       REACTION:  1.0 BAO      +  1.0 MOO3     --->  1.0 (BA    ))(MOO4 ))

         OXIDE                   A              B               D           TEMPERATURE RANGE
                                                                            DEGREES CENTIGRADE

CATION   BAO                1.2733+01      1.0392-03       1.9829+05      2.5000+01 TO  7.0000+02
ANION    MOO3               2.0060+01      5.8984-03       3.6791+05      2.5000+01 TO  7.0000+02

             ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                           HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                       REACTION:  1.0 BAO      +  1.0 MOO3     --->  1.0 (BA    ))(MOO4 ))


            A              B              D             TEMPERATURE  RANGE        RMS  ERROR
                                                         DEGREES CENTIGRADE

        3.2794+01      6.9377-03      5.6619+05      2.5000+01 TO  7.0000+02      9.6278-05


MIXED METAL OXIDE          A              B              D              TEMPERATURE  RANGE     RMS  ERROR
                                                                        DEGREES CENTIGRADE

(BA    ))(MOO4 ))      3.2794+01      6.9377-03      5.6618+05      2.5000+01 TO  7.0000+02   9.6278-05
```

```
              HEAT CAPACITIES OF CONSTITUENT OXIDES IN CALORIES/ GMOLE/ DEGREES KELVIN

                        HEAT CAPACITY EQUATION    CP= A + B*T - D/(T**2)


                    REACTION:  1.0 BAO      +  1.0 AL2O3    --->  1.0 (BA    ))(AL2O4))

          OXIDE                  A              B               D              TEMPERATURE RANGE
                                                                               DEGREES CENTIGRADE

CATION    BAO                1.2733+01      1.0392-03       1.9829+05      2.5000+01 TO  7.0000+02
ANION     AL2O3              2.6405+01      4.3400-03       7.9230+05      2.5000+01 TO  7.0000+02

          ESTIMATED HEAT CAPACITIES OF MIXED METAL OXIDES IN CALORIES / GMOLE / DEGREES KELVIN

                         HEAT CAPACITY EQUATION  CP = A + B*T - D/(T**2)

                    REACTION:  1.0 BAO      +  1.0 AL2O3    --->  1.0 (BA    ))(AL2O4))


                 A              B               D            TEMPERATURE  RANGE        RMS  ERROR
                                                             DEGREES CENTIGRADE

             3.9138+01      5.3792-03       9.9059+05      2.5000+01 TO  7.0000+02       7.6912-05



MIXED METAL OXIDE          A              B               D              TEMPERATURE  RANGE     RMS  ERROR
                                                                         DEGREES CENTIGRADE

(BA    ))(AL2O4))      3.9138+01      5.3792-03       9.9057+05      2.5000+01 TO  7.0000+02   7.6912-05
```

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

23 December 1968 T. Parsons

TECHNICAL MEMORANDUM 004-009-Ch13

ESTIMATION OF HEAT CAPACITIES FOR METAL SULFIDES

I. INTRODUCTION

This memorandum describes the estimation of heat capacities for metal sulfides by the addition of a small increment, ΔCp, to the corresponding metal oxide heat capacities. The increment ΔCp was calculated from known sulfide and oxide heat capacity data found in the TRACOR data base. The error in estimated heat capacities was minimized using a least squares technique and the accuracy of the estimated quantities is described in relation to the known sulfide heat capacities.

II. MATHEMATICAL DESCRIPTION OF THE METHOD

Let the heat capacity of metal oxide Me_xO_y be illustrated by Equation 1a and the heat capacity of metal sulfide Me_xS_y be illustrated by Equation 1b.

$$Cp_0 = a_0 + b_0T - d_0/T^2 \qquad (1a)$$

$$Cp_S = a_S + b_ST - d_S/T^2 \qquad (1b)$$

Equation 2 defines ΔCp on a per mole of sulfide basis.

$$\Delta Cp = \Delta a + \Delta bT - \Delta d/T^2 \qquad (2)$$

In general, the estimation method is described by Equations 3a and 3b, where y is the number of S or 0 atoms combined with the metal.

$$Cp_S = Cp_0 + y\Delta Cp \qquad (3a)$$

$$Cp_S = (a_0 + y\Delta a) + (b_0 + y\Delta b)T - (d_0 + y\Delta d)/T^2 \qquad (3b)$$

The increment to be added to the oxide heat capacity, $y\Delta Cp$, is described for each of the J sulfide-oxide pairs by Equations 4a and 4b. The actual ΔCp will be a function of all of the ΔCp's for each of the J oxide-sulfide pairs.

$$y\Delta Cp_j = Cp_{0_j} - Cp_{S_j} \qquad (4a)$$

$$\Delta Cp_j = \frac{1}{y}\left[(a_{0_j} - a_{S_j}) + (b_{0_j} - b_{S_j})T - (d_{0_j} - d_{S_j})/T^2\right] \qquad (4b)$$

Equation 5a gives the difference, E, between the estimated and accepted values for sulfide heat capacity.

$$E = Cp_S - (Cp_0 + y\Delta Cp) \qquad (5a)$$

The error per mole of sulfide, Δ, in the estimated heat capacity is then given by Equations 5b and 5c.

$$\Delta = (\frac{1}{y})E = \frac{1}{y}CP_S - (\frac{1}{y}Cp_0 + \Delta Cp) \qquad (5b)$$

$$\Delta = \left[\frac{1}{y}(a_0 - a_S) - \Delta a\right] + \left[\frac{1}{y}(b_0 - b_S) - \Delta b\right]T - \left[\frac{1}{y}(d_0 - d_S) - \Delta d\right]/T^2 \qquad (5c)$$

Equation 5 can be simplified by substituting A, B, and D, as described by Equations 6, 7, and 8.

$$A = \frac{1}{y}(a_0 - a_S) \qquad (6)$$

$$B = \frac{1}{y}(b_0 - b_S) \qquad (7)$$

$$D = \frac{1}{y}(d_0 - d_S) \qquad (8)$$

Technical Memorandum 004-009-Ch9 was concerned with heat capacity estimations for mixed metal oxides. In that memorandum we discussed the concept of a valid temperature range for the sum of two heat capacity coefficients. The same ideas are true for the difference of two heat capacity coefficients. We must provide for the fact that the metal oxide and metal sulfide heat capacities may have different temperature ranges of validity, and that the difference in the sulfide and oxide heat capacities will have a particular temperature range of validity. The valid range will again be the interval for which there are data for both the sulfide and oxide.

Furthermore, as discussed in Technical Memorandum 004-009-Ch9, the fact that the metal oxide has a transition, and therefore a new set of heat capacity coefficients, is no guarantee that the corresponding sulfide should also have one. Therefore we wish to calculate the best single set of coefficients that describe ΔCp for all temperatures and all corresponding oxide-sulfide pairs (data points).

In light of these considerations, we recognize that for each of the j data sets (sulfide-oxide pairs) there will be I_j temperature intervals. In each interval there will be a true value of A, called A_{ij}, as described by Equation 9.

$$A_{ij} = \frac{1}{y_j} (a_{O_i} - a_{S_i})_j \tag{9}$$

The same is true for B and D (Equations 10 and 11).

$$B_{ij} = \frac{1}{y_j} (b_{O_i} - b_{S_i})_j \tag{10}$$

$$D_{ij} = \frac{1}{y_j} (d_{O_i} - d_{S_i})_j \tag{11}$$

Equation 5c is now written as Equation 12.

$$\Delta_{ij} = (A_{ij} - \Delta a) + (B_{ij} - \Delta b)T - (D_{ij} - \Delta d)/T^2 \tag{12}$$

Our problem is to calculate a single set of coefficients, Δa, Δb, and Δd which gives the best value of ΔCp for all sulfide-oxide pairs and which is valid over the whole temperature range of interest. Therefore, we can describe the squared error for one sulfide-oxide pair, Δ^2, by Equation 13.

$$\Delta_j^2 = \sum_{i=1}^{I_j} \int_{T_{i-1}}^{T_i} [(A_{ij} - \Delta a) + (B_{ij} - \Delta b)T - (D_{ij} - \Delta d)/T^2]^2 \, dT \tag{13}$$

Since we have more than one sulfide-oxide heat capacity difference, we wish to sum all the errors for each data set. If there were J sulfide-oxide pairs, the squared error per mole of sulfide for all data sets would be written as Equation 14.

$$\Delta^2 = \sum_{j=1}^{J} \sum_{i=1}^{I_j} \int_{T_{i-1}}^{T_i} [(A_{ij} - \Delta a) + (B_{ij} - \Delta b)T - (D_{ij} - \Delta d)/T^2]^2 \, dT \tag{14}$$

The conditions necessary for the squared error to be a minimum are given by Equations 15, 16, and 17.

$$\frac{\partial \Delta^2}{\partial \Delta a} = 0 \tag{15}$$

$$\frac{\partial \Delta^2}{\partial \Delta b} = 0 \tag{16}$$

$$\frac{\partial \Delta^2}{\partial \Delta d} = 0 \tag{17}$$

The derivatives and integrals in Equations 14, 15, 16, and 17 are of the same form as Equations 7 , 8, 9, and 10 in T.M. 004-009-Ch9. The results are given in Equations 18, 19, and 20.

$$\begin{aligned}\Delta a \sum_{j=1}^{J} (T_{I_j} - T_{0_j}) + \Delta b \sum_{j=1}^{J} \frac{\left(T^2_{I_j} - T^2_{0_j}\right)}{2} + \Delta d \sum_{j=1}^{J} \left(\frac{1}{T_{I_j}} - \frac{1}{T_{0_j}} \right) \\ = \sum_{j=1}^{J} \sum_{i=1}^{I_j} \left[A_{ij} \, (T_i - T_{i-1})_j + B_{ij} \frac{\left(T_i^2 - T_{i-1}^2\right)_j}{2} + D_{ij} \left(\frac{1}{T_i} - \frac{1}{T_{i-1}}\right)_j \right]\end{aligned} \tag{18}$$

$$\Delta a \sum_{j=1}^{J} \frac{\left(T_{I_j}^2 - T_{0_j}^2\right)}{2} + \Delta b \sum_{j=1}^{J} \frac{\left(T_{I_j}^3 - T_{0_j}^3\right)}{3} - \Delta d \sum_{j=1}^{J} \ln \frac{T_{I_j}}{T_{0_j}}$$

$$= \sum_{j=1}^{J} \sum_{i=1}^{I_j} \left[A_{ij} \frac{\left(T_i^2 - T_{i-1}^2\right)_j}{2} + B_{ij} \frac{\left(T_i^3 - T_{i-1}^3\right)_j}{3} - D_{ij} \ln \left(\frac{T_i}{T_{i-1}} \right)_j \right] \qquad (19)$$

$$\Delta a \sum_{j=1}^{J} \left(\frac{1}{T_{I_j}} - \frac{1}{T_{0_j}} \right) - \Delta b \sum_{j=1}^{J} \ln \left(\frac{T_{I_j}}{T_{0_j}} \right) - \frac{\Delta d}{3} \sum_{j=1}^{J} \left(\frac{1}{T_{I_j}^3} - \frac{1}{T_{0_j}^3} \right) \qquad (20)$$

$$= \sum_{j=1}^{J} \sum_{i=1}^{I_j} \left[A_{ij} \left(\frac{1}{T_i} - \frac{1}{T_{i-1}} \right)_j - B_{ij} \ln \left(\frac{T_i}{T_{i-1}} \right)_j - \frac{D_{ij}}{3} \left(\frac{1}{T_i^3} - \frac{1}{T_{i-1}^3} \right)_j \right]$$

Equations 18, 19, and 20 can be solved for Δa, Δb, and Δd.

The root mean square (RMS) error for the calculation of Δa, Δb, and Δd is given in Equation 21.

$$\mathrm{RMS} = \left\{ \frac{1}{\sum_{j=1}^{J} (T_{I_j} - T_{0_j})} \sum_{j=1}^{J} \sum_{i=1}^{I_j} \int_{T_{ij-1}}^{T_{ij}} [A_{ij} - \Delta a + (B_{ij} - \Delta b)T - (D_{ij} - \Delta d)/T^2]^2 \, dT \right\}^{\frac{1}{2}} \qquad (21)$$

In this case the RMS will tell us how close we came in calories to estimating the heat capacity of metal sulfides. We would have more information if we could see the error in our estimation in relation to the magnitude of the known heat capacities. Therefore, we are interested in the fractional error, F. The fractional error is defined as the RMS error divided by the average sulfide heat capacity $\overline{Cp_S}$. $\overline{Cp_S}$ is defined by Equation 22.

$$\overline{Cp_S} = \frac{1}{\sum_{j=1}^{J} (T_{I_j} - T_{0_j})_S} \sum_{j=1}^{J} \frac{1}{y_j} \sum_{i=1}^{I_j} \int_{T_{i-1}}^{T_i} (a_S + b_S T - d_S/T^2) \, dT \qquad (22)$$

Note that the inverse temperature interval sums in Equations 21 and 22 are not identical. The difference $(T_{I_j} - T_{0_j})$ in Equation 21 refers to the temperature range of the sulfide-oxide pairs while the difference $(T_{I_j} - T_{0_j})_S$ in Equation 22 refers to the temperature range for the sulfide heat capacity. Finally, by definition, the fractional error, F, is written as Equation 23.

$$F = \mathrm{RMS} / \overline{Cp_s} \qquad (23)$$

III. RESULTS

Heat capacities of metal sulfides for which there exist no data were estimated by adding the increment ΔCp, described by Equation 24, to the heat capacity equation for the corresponding metal oxide.

$$\Delta Cp = 1.86 - 1.12 \times 10^{-3} T - 0.214 \times 10^{5}/T^{2} \qquad (24)$$

The values of Δa, Δb, and Δd were calculated by the method discussed in Section II. The values are based on heat capacity data for Ag_2S, Bi_2S_3, CdS, FeS, MgS, MnS, Na_2S, PbS, Sb_2S_3, SnS, SnS_2, TiS_2, US_2, and ZnS. These data are found in the TRACOR data base and are shown in Table I. The fractional error for the ΔCp calculation was 0.0652.

Values for heat capacities of metal oxides are in Table II. From these metal oxide heat capacities, sulfide heat capacities were estimated by adding yΔCp, where y indicates the number of S atoms or O atoms combined with the metal to form the sulfide or oxide.

As in the case of the mixed metal oxides, the fact that the metal oxide has more than one set of coefficients, each for a particular temperature interval, does not guarantee that the sulfide coefficients should also change. Therefore, the calculations described in Section II of T.M. 004-009-Ch9 were carried out to obtain a single set of coefficients for the metal sulfide heat capacity which would be valid over the range of interest. In this case, since ΔCp is valid for all temperature intervals, the temperature range of validity for the estimated sulfide heat capacity is that range for which there are oxide data.

The estimated sulfide heat capacities are in Table III. If there were no experimentally obtained data available, the estimated values were added to the TRACOR data base with a reference to this memorandum.

J. Parsons

TABLE I

ACCEPTED VALUES FOR METAL SULFIDE HEAT CAPACITIES

TABLE I

COMPOUNDS WITH KNOWN SULFIDE HEAT CAPACITIES

1	AG2O	AG2S	1.00
2	BI2O3	BI2S3	3.00
3	CDO	CDS	1.00
4	FEO	FES	1.00
5	MGO	MGS	1.00
6	MNO	MNS	1.00
7	NA2O	NA2S	1.00
8	PBO	PBS	1.00
9	SB2O3	SB2S3	3.00
10	SNO	SNS	1.00
11	SNO2	SNS2	2.00
12	TIO2	TIS2	2.00
13	UO2	US2	2.00
14	ZNO	ZNS	1.00

TABLE I (continued)

ACCEPTED VALUES OF METAL SULFIDE HEAT CAPACITIES
CAL./ GMOLE/ DEG.KELVIN
CP = A + BT - D/T**2

	METAL SULFIDE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
1	AG2S	1.013000+01	2.640000-02	0.000000	2.500000+01 TO 1.790000+02
		2.164000+01	0.000000	0.000000	1.790000+02 TO 5.770000+02
2	BI2S3	2.889000+01	6.097000-03	5.490000+02	2.500000+01 TO 6.000000+02
3	CDS	1.293000+01	8.670000-04	3.520000+02	2.500000+01 TO 7.000000+02
4	FES	5.190000+00	2.640000-02	0.000000	2.500000+01 TO 1.380000+02
		1.740000+01	0.000000	0.000000	1.380000+02 TO 3.250000+02
		1.220000+01	2.380000-03	0.000000	3.250000+02 TO 1.195000+03
5	MGS	9.240000+00	2.500000-03	-7.930000+02	2.500000+01 TO 7.000000+02
6	MNS	1.139553+01	1.798917-03	0.000000	2.500000+01 TO 1.200000+03
7	NA2S	1.981000+01	1.640000-03	0.000000	2.500000+01 TO 7.270000+02
8	PBS	1.066000+01	3.920000-03	0.000000	2.500000+01 TO 6.000000+02
9	SB2S3	2.420000+01	1.320000-02	0.000000	2.500000+01 TO 5.250000+02
10	SNS	8.479500+00	7.428000-03	-9.526000+04	2.500000+01 TO 5.840000+02
		9.775768+00	3.738785-03	0.000000	5.840000+02 TO 8.800000+02
11	SNS2	1.551000+01	4.197000-03	9.630000+01	2.500000+01 TO 7.000000+02
12	TIS2	8.080000+00	2.734000-02	0.000000	2.500000+01 TO 1.470000+02
		1.499000+01	5.140000-03	0.000000	1.470000+02 TO 7.370000+02
13	US2	1.520000+01	8.700000-03	0.000000	2.500000+01 TO 3.520000+02
14	ZNS	1.216000+01	1.236000-03	1.361000+05	2.500000+01 TO 9.270000+02

TABLE II

METAL OXIDE HEAT CAPACITIES

TABLE II

COMPOUNDS FOR WHICH SULFIDE HEAT CAPACITIES ARE TO BE ESTIMATED

1	AL2O3	AL2S3	3.00
2	AS2O3	AS2S3	3.00
3	B2O3	B2S3	3.00
4	BAO	BAS	1.00
5	BEO	BES	1.00
6	CAO	CAS	1.00
7	CEO2	CES2	2.00
8	CE2O3	CE2S3	3.00
9	COO	COS	1.00
10	CO3O4	CO3S4	4.00
11	CRO3	CRS3	3.00
12	CR2O3	CR2S3	3.00
13	CUO	CUS	1.00
14	GA2O3	GA2S3	3.00
15	GEO2	GES2	2.00
16	HFO2	HFS2	2.00
17	IRO2	IRS2	2.00
18	LA2O3	LA2S3	3.00
19	LI2O	LI2S	1.00
20	MNO2	MNS2	2.00
21	MN2O3	MN2S3	3.00
22	MOO3	MOS3	3.00
23	NA2O	NA2S	1.00
24	NB2O5	NB2S5	5.00
25	NIO	NIS	1.00
26	PBO2	PBS2	2.00
27	PDO	PDS	1.00
28	RHO	RHS	1.00
29	RH2O	RH2S	1.00
30	RH2O3	RH2S3	3.00
31	SC2O3	SC2S3	3.00
32	SIO2	SIS2	2.00
33	SRO	SRS	1.00
34	TA2O5	TA2S5	5.00
35	THO2	THS2	2.00
36	TIO	TIS	1.00
37	TI2O3	TI2S3	3.00
38	VO	VS	1.00
39	V2O3	V2S3	3.00

TABLE II (continued)

40	V204	V2S4	4.00
41	V205	V2S5	5.00
42	W02	WS2	2.00
43	Y203	Y2S3	3.00
44	ZR02	ZRS2	2.00

TABLE II (continued)

METAL OXIDE HEAT CAPACITIES
CAL./ GMOLE/ DEG.KELVIN
CP = A + BT - D/T**2

	METAL OXIDE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
1	AG2O	1.325417+01	7.037994-03	0.000000	2.500000+01 TO 7.000000+02
2	BI2O3	2.472615+01	7.995983-03	0.000000	2.500000+01 TO 5.000000+02
3	CDO	9.646782+00	2.078430-03	0.000000	2.500000+01 TO 7.000000+02
4	FEO	1.165593+01	1.999593-03	7.597020+04	2.500000+01 TO 1.200000+03
5	MGO	1.017475+01	1.739192-03	1.478791+05	2.500000+01 TO 1.727000+03
6	MNO	1.110407+01	1.939868-03	8.791520+04	2.500000+01 TO 1.200000+03
7	NA2O	1.569334+01	5.396751-03	0.000000	2.500000+01 TO 7.000000+02
8	PBO	1.059521+01	3.999186-03	0.000000	2.500000+01 TO 6.000000+02
9	SB2O3	1.908811+01	1.708135-02	0.000000	2.500000+01 TO 9.000000+02
10	SNO	9.546444+00	3.497496-03	0.000000	2.500000+01 TO 7.000000+02
11	SNO2	1.765232+01	2.398556-03	5.157851+05	2.500000+01 TO 1.200000+03
12	TIO2	1.713152+01	9.794900-04	3.497496+05	2.500000+01 TO 1.200000+03
13	UO2	1.919084+01	1.619742-03	3.956184+05	2.500000+01 TO 1.200000+03
14	ZNO	1.170371+01	1.218390-03	2.178768+05	2.500000+01 TO 1.200000+03
15	AL2O3	2.640500+01	4.340000-03	7.923000+05	2.500000+01 TO 7.000000+02
16	AS2O3	8.370000+00	4.860000-02	0.000000	2.500000+01 TO 3.000000+02

TABLE II (continued)

	METAL OXIDE	METAL OXIDE HEAT CAPACITIES (CONTINUED) A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
17	B2O3	8.727017+00	2.539507-02	1.309172+05	2.500000+01 TO 7.000000+02
18	BAO	1.273337+01	1.039215-03	1.982870+05	2.500000+01 TO 7.000000+02
19	BEO	8.445115+00	3.999186-03	3.167814+05	2.500000+01 TO 7.000000+02
20	CAO	1.185661+01	1.079828-03	1.660355+05	2.270000+02 TO 6.270000+02
21	CEO2	1.500292+01	2.508450-03	0.000000	2.500000+01 TO 1.700000+03
22	CE2O3	2.517000+01	6.327000-03	0.000000	3.000000+02 TO 8.400000+02
23	COO	1.153409+01	2.040206-03	-3.989630+04	2.500000+01 TO 1.200000+03
24	CO3O4	3.081810+01	1.707179-02	5.757490+05	2.500000+01 TO 7.000000+02
25	CRO3	2.128500+01	5.399500-03	4.957000+05	2.500000+01 TO 7.000000+02
26	CR2O3	2.852466+01	2.197880-03	3.738785+05	2.500000+01 TO 1.200000+03
27	CUO	9.266931+00	4.797112-03	0.000000	2.500000+01 TO 7.000000+02
28	GA2O3	1.176582+01	2.518006-02	0.000000	2.500000+01 TO 6.000000+02
29	GEO2	1.119485+01	7.167000-03	0.000000	2.500000+01 TO 7.070000+02
30	HFO2	1.738236+01	2.078430-03	3.478384+05	2.500000+01 TO 1.200000+03
31	IRO2	9.166593+00	1.519404-02	0.000000	2.500000+01 TO 7.000000+02
32	LA2O3	2.885912+01	3.074643-03	3.268152+05	2.500000+01 TO 7.000000+02
33	LI2O	1.493244+01	6.077616-03	3.378046+05	2.500000+01 TO 7.000000+02
34	MNO2	1.659160+01	2.439169-03	3.877347+05	2.500000+01 TO 5.000000+02

TABLE II (continued)

METAL OXIDE HEAT CAPACITIES (CONTINUED)

	METAL OXIDE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
35	MN203	2.472615+01	8.375834-03	3.227539+05	2.500000+01 TO 7.000000+02
36	MOO3	2.006043+01	5.898441-03	3.679060+05	2.500000+01 TO 7.000000+02
37	NA20	1.569334+01	5.396751-03	0.000000	2.500000+01 TO 7.000000+02
38	NB205	3.621724+01	5.537702-03	4.878338+05	2.500000+01 TO 1.200000+03
39	NIO	-4.988232+00	3.755508-02	-3.889292+05	2.500000+01 TO 2.500000+02
		1.117574+01	2.018705-03	0.000000	2.500000+02 TO 1.200000+03
40	PBO2	1.269515+01	7.797696-03	0.000000	2.500000+01 TO 7.000000+02
41	PDO	3.299209+00	1.419305-02	0.000000	2.500000+01 TO 5.000000+02
42	RHO	9.835513+00	5.528146-03	0.000000	2.500000+01 TO 7.000000+02
43	RH20	1.560495+01	6.467023-03	0.000000	2.500000+01 TO 9.000000+02
44	RH203	2.071980+01	1.378453-02	0.000000	2.500000+01 TO 9.000000+02
45	SC203	2.315897+01	5.638040-03	0.000000	2.500000+01 TO 1.700000+03
46	SIO2	1.121397+01	8.196659-03	2.699570+05	2.500000+01 TO 8.670000+02
		1.440328+01	1.939868-03	0.000000	8.670000+02 TO 1.610000+03
47	SRO	1.233441+01	1.120441-03	1.806084+05	2.500000+01 TO 7.000000+02
48	TA205	3.698172+01	6.557805-03	5.946221+05	2.500000+01 TO 1.200000+03
49	THO2	1.583190+01	2.878745-03	1.598241+05	2.500000+01 TO 1.200000+03
50	TIO	1.056416+01	3.597834-03	1.858642+05	2.500000+01 TO 9.910000+02
		1.184466+01	3.010140-03	0.000000	9.910000+02 TO 1.200000+03

TABLE II (continued)

METAL OXIDE HEAT CAPACITIES (CONTINUED)

	METAL OXIDE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
51	TI203	7.307951+00	5.348971-02	0.000000	2.500000+01 TO 2.000000+02
		3.466439+01	1.299616-03	1.067405+06	2.000000+02 TO 1.200000+03
52	VO	1.131430+01	3.217983-03	1.259003+05	2.500000+01 TO 1.200000+03
53	V203	2.933692+01	4.758888-03	5.418252+05	2.500000+01 TO 1.200000+03
54	V204	2.988639+01	0.000000	0.000000	2.500000+01 TO 7.200000+01
		3.569166+01	3.447327-03	7.886089+05	7.200000+01 TO 1.200000+03
55	V205	4.651383+01	3.898848-03	1.321356+06	2.500000+01 TO 6.700000+02
		4.558212+01	0.000000	0.000000	6.700000+02 TO 1.200000+03
56	WO2	1.783000+01	1.890000-03	3.342000+05	2.500000+01 TO 1.200000+03
57	Y203	2.960000+01	1.200000-03	4.780000+05	2.500000+01 TO 1.000000+03
58	ZRO2	1.663222+01	1.798917-03	3.358934+05	2.500000+01 TO 7.000000+02

TABLE III

ESTIMATED SULFIDE HEAT CAPACITIES

TABLE III

ESTIMATED VALUES OF METAL SULFIDE HEAT CAPACITIES

CAL./ GMOLE/ DEG.KELVIN

CP = CP(OXIDE) + DELTA CP

DELTA CP = 1.8636+00 + -1.1207-03*T - -2.1421+04/T**2

	METAL SULFIDE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE
1	AG2S	1.511780+01	5.917320-03	-2.142141+04	2.500000+01 TO 7.000000+02
2	BI2S3	3.031705+01	4.633961-03	-6.426422+04	2.500000+01 TO 5.000000+02
3	CDS	1.151041+01	9.577559-04	-2.142141+04	2.500000+01 TO 7.000000+02
4	FES	1.351956+01	8.789189-04	5.454879+04	2.500000+01 TO 1.200000+03
5	MGS	1.203838+01	6.185179-04	1.264577+05	2.500000+01 TO 1.727000+03
6	MNS	1.296770+01	8.191939-04	6.649379+04	2.500000+01 TO 1.200000+03
7	NA2S	1.755697+01	4.276077-03	-2.142141+04	2.500000+01 TO 7.000000+02
8	PBS	1.245885+01	2.878512-03	-2.142141+04	2.500000+01 TO 6.000000+02
9	SB2S3	2.467901+01	1.371933-02	-6.426422+04	2.500000+01 TO 9.000000+02
10	SNS	1.141008+01	2.376822-03	-2.142141+04	2.500000+01 TO 7.000000+02
11	SNS2	2.137958+01	1.572079-04	4.729423+05	2.500000+01 TO 1.200000+03
12	TIS2	2.085878+01	-1.261858-03	3.069068+05	2.500000+01 TO 1.200000+03
13	US2	2.291810+01	-6.216061-04	3.527756+05	2.500000+01 TO 1.200000+03
14	ZNS	1.356734+01	9.771595-05	1.964554+05	2.500000+01 TO 1.200000+03
15	AL2S3	3.199590+01	9.779779-04	7.280358+05	2.500000+01 TO 7.000000+02
16	AS2S3	1.396090+01	4.523798-02	-6.426422+04	2.500000+01 TO 3.000000+02

TABLE III (continued)

17	B2S3	1.431791+01	2.203305-02	6.665298+04	2.500000+01	TO	7.000000+02
18	BAS	1.459700+01	-8.145905-05	1.768656+05	2.500000+01	TO	7.000000+02
19	BES	1.030875+01	2.878512-03	2.953600+05	2.500000+01	TO	7.000000+02
20	CAS	1.372024+01	-4.084605-05	1.446141+05	2.270000+02	TO	6.270000+02
21	CES2	1.873018+01	2.671019-04	-4.284281+04	2.500000+01	TO	1.700000+03
22	CE2S3	3.076090+01	2.964978-03	-6.426422+04	3.000000+02	TO	8.400000+02
23	COS	1.339772+01	9.195319-04	-6.131771+04	2.500000+01	TO	1.200000+03
24	CO3S4	3.827263+01	1.258910-02	4.900634+05	2.500000+01	TO	7.000000+02
25	CRS3	2.687590+01	2.037478-03	4.314358+05	2.500000+01	TO	7.000000+02
26	CR2S3	3.411556+01	-1.164142-03	3.096143+05	2.500000+01	TO	1.200000+03
27	CUS	1.113056+01	3.676438-03	-2.142141+04	2.500000+01	TO	7.000000+02
28	GA2S3	1.735672+01	2.181804-02	-6.426422+04	2.500000+01	TO	6.000000+02
29	GES2	1.492212+01	4.925652-03	-4.284281+04	2.500000+01	TO	7.070000+02
30	HFS2	2.110963+01	-1.629181-04	3.049956+05	2.500000+01	TO	1.200000+03
31	IRS2	1.289386+01	1.295269-02	-4.284281+04	2.500000+01	TO	7.000000+02
32	LA2S3	3.445002+01	-2.873791-04	2.625510+05	2.500000+01	TO	7.000000+02
33	LI2S	1.679608+01	4.956942-03	3.163832+05	2.500000+01	TO	7.000000+02
34	MNS2	2.031887+01	1.978209-04	3.448919+05	2.500000+01	TO	5.000000+02
35	MN2S3	3.031705+01	5.013812-03	2.584897+05	2.500000+01	TO	7.000000+02

TABLE III (continued)

36	MOS3	2.565133+01	2.536419-03	3.036418+05	2.500000+01	TO	7.000000+02
37	NA2S	1.755697+01	4.276077-03	-2.142141+04	2.500000+01	TO	7.000000+02
38	NB2S5	4.553540+01	-6.566819-05	3.807268+05	2.500000+01	TO	1.200000+03
39	NIS	1.468008+01	-4.176385-04	1.098033+05	2.500000+01	TO	1.200000+03
40	PBS2	1.642241+01	5.556348-03	-4.284281+04	2.500000+01	TO	7.000000+02
41	PDS	5.162841+00	1.307237-02	-2.142141+04	2.500000+01	TO	5.000000+02
42	RHS	1.169914+01	4.407472-03	-2.142141+04	2.500000+01	TO	7.000000+02
43	RH2S	1.746858+01	5.346349-03	-2.142141+04	2.500000+01	TO	9.000000+02
44	RH2S3	2.631069+01	1.042251-02	-6.426422+04	2.500000+01	TO	9.000000+02
45	SC2S3	2.874986+01	2.276018-03	-6.426422+04	2.500000+01	TO	1.700000+03
46	SIS2	2.279823+01	-2.855129-03	8.601892+05	2.500000+01	TO	1.610000+03
47	SRS	1.419804+01	-2.330344-07	1.591870+05	2.500000+01	TO	7.000000+02
48	TA2S5	4.629988+01	9.544349-04	4.875151+05	2.500000+01	TO	1.200000+03
49	THS2	1.955917+01	6.373969-04	1.169813+05	2.500000+01	TO	1.200000+03
50	TIS	1.170874+01	3.248971-03	1.038532+05	2.500000+01	TO	1.200000+03
51	TI2S3	4.060767+01	-2.352530-03	1.022974+06	2.500000+01	TO	1.200000+03
52	VS	1.317794+01	2.097309-03	1.044789+05	2.500000+01	TO	1.200000+03
53	V2S3	3.492782+01	1.396866-03	4.775610+05	2.500000+01	TO	1.200000+03
54	V2S4	4.266768+01	-6.861142-04	6.154419+05	2.500000+01	TO	1.200000+03

TABLE III (continued)

55	V2S5	6.317079+01	-1.106329-02	1.726434+06	2.500000+01 TO 1.200000+03
56	WS2	2.155726+01	-3.513480-04	2.913572+05	2.500000+01 TO 1.200000+03
57	Y2S3	3.519090+01	-2.162022-03	4.137358+05	2.500000+01 TO 1.000000+03
58	ZRS2	2.035948+01	-4.424311-04	2.930506+05	2.500000+01 TO 7.000000+02

RMS ERROR / AVERAGE SULFIDE HEAT CAPACITIY = FRACTIONAL ERROR = 6.5153-02

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

20 June 1969 Terry Parsons

TECHNICAL MEMORANDUM 004-009-Ch13A

ESTIMATION OF HEAT CAPACITY FOR INORGANIC SALTS

INTRODUCTION

This memorandum is concerned with the estimation of heat capacity equations of the form $A + BT - D/T^2$ for inorganic solids. The method has been described for estimating the heat capacity of metal sulfides in T.M. 004-009-Ch13. This memorandum is a description of the method for the "general" case. The results for sulfates, sulfites, carbonates and sulfides are included. There are two basic methods relied on in heat capacity estimation. The first, Dulong and Petit's rule, states that the atomic heat at constant pressure, Cp, of an element is generally 6.2 - 6.5 cal/deg per atom at room temperature. It is also recognized that the heat capacity increases to a value that is roughly constant for all elements, 7.0 to 7.25 cal/deg per atom, at the temperature of the first transition. This rule may be applied to the estimation of heat capacities if the temperature or entropy of the first transition is known. Since these data are unknown for many of the compounds of interest, our estimation method is based on the second basic method, the rule of Neumann and Kopp that the heat capacity of a solid is equal to the sum of the heat capacities of the constituent elements. This rule is reliable as long as the rule of Dulong and Petit holds for the elements.

SELECTION OF THE METHOD

The problem was to find the best way of applying Kopp's rule for the compounds of interest. There were two choices. Consider, for example, the heat capacity of a metal sulfate. The heat capacity could be estimated by (1) adding the heat capacity of the metal oxide and the SO_3 "lattice" contribution, or (2) adding the heat capacity of the metal and the $SO_4^=$ anion heat capacity contribution. In the first case the SO_3 lattice contribution could be obtained by subtracting a metal oxide heat capacity from the corresponding metal sulfate heat capacity for many sulfate-oxide combinations. In the second, the $SO_4^=$ anion contribution could be obtained by subtracting the metal Cp from its corresponding sulfate Cp for several sulfate-oxide combinations. A third modification could be obtained by calculating an $SO_4^=$ anion contribution for the sulfate of an element in a particular periodic subgroup and applying it only to the next element in that subgroup instead of obtaining an average $SO_4^=$ anion contribution. A problem involved in the second and third methods is that metals often have low-temperature melting or transition points.

These three methods were applied to the estimation of known sulfate, carbonate, and sulfite heat capacities. The RMS errors were 1.58, 2.05, and 3.80 cal/deg mole for methods 1, 2, and 3, respectively.

The first method was selected as the best on the basis of its accuracy and applicability. The method of subtracting metal oxide heat capacities from the heat capacity of another salt of the same metal and obtaining a constant contribution for the remaining lattice was found to be widely applicable. It was used for estimating the heat capacities of sulfates, sulfites, carbonates, sulfides and mixed oxides and has been shown to be valid for nitrates and nitrites. In the case of the mixed oxides the process was reduced to the simple addition of two metal oxide heat capacities.

MATHEMATICAL DESCRIPTION OF THE METHOD

The following is a general mathematical description of the least squares technique used to obtain the best value for the contribution to be added to the oxide heat capacity to estimate that of other salts.

The constant increment, $\overline{\Delta}$, to be added to the metal oxide heat capacity can be obtained for the J metal salt-metal oxide combinations by subtracting the heat capacity equation of the oxide (Equation 1) from that of the Salt S (Equation 2).

$$Cp_{o_j} = a_o + b_oT - d_o/T^2 \qquad (1)$$

$$Cp_{s_j} = a_s + b_sT - d_s/T^2 \qquad (2)$$

This subtraction is shown in Equation 3.

$$\Delta j = (a_s - a_o)_j + (b_s - b_o)_jT - (d_s - d_o)_j/T^2 \qquad (3)$$

The estimated heat capacity for any metal salt is given in Equation 4 where $\overline{\Delta} = \overline{\Delta}a + \overline{\Delta}bT - \overline{\Delta}d/T^2$.

$$Cp_{s_j} = Cp_{o_j} + \overline{\Delta} \qquad (4)$$

The value of $\overline{\Delta}$ depends on all the Δj's, each of which may have several different forms valid over I different temperature ranges, depending on the transition temperatures of the J$^{th.}$ metal oxide and metal salt. Thus, for any metal oxide-metal salt combination J, there may be I different ranges of validity for Δj, and therefore, I values of Δj. We can then rewrite Δj as Δij according to Equation 5.

$$\begin{aligned} \Delta ij &= (a_{s_i} - a_{o_i}) + (b_{s_i} - b_{o_i})T - (d_{s_i} - d_{o_i})/T^2 \\ &= (A_{i_j} + B_{i_j}T - D_{i_j}/T^2) \qquad (5) \end{aligned}$$

All Δij combinations were weighted linearly throughout the temperature range to determine the optimum value of $\bar{\Delta}$. This corresponds to integration. The squared error, E^2, in the estimated heat capacity is then shown for all ij combinations in in Equation 6.

$$\begin{aligned} E^2 &= \sum_{j=1}^{J} \sum_{i=1}^{I_j} \int_{T_{ij-1}}^{T_{ij}} \left[Cp_{s_{ij}} - \left(Cp_{o_{ij}} + \bar{\Delta} \right) \right]^2 dT \\ &= \sum_{j=1}^{J} \sum_{i=1}^{I_j} \int_{T_{ij-1}}^{T_{ij}} \left[\left(a_{s_{ij}} - a_{o_{ij}} - \bar{\Delta}a \right) + \left(b_{s_{ij}} - b_{o_{ij}} - \bar{\Delta}b \right) T \right. \\ &\qquad \left. - \left(d_{s_{ij}} - d_{o_{ij}} - \bar{\Delta}d \right) / T^2 \right]^2 dT \qquad (6) \end{aligned}$$

$$= \sum_{j=1}^{J} \sum_{i=1}^{I_j} \int_{T_{ij-1}}^{T_{ij}} \left[A_{ij} - \overline{\Delta}a + \left(B_{ij} - \overline{\Delta}b\right) T - \left(D_{ij} - \overline{\Delta}d\right)/T^2 \right]^2 dT \qquad (6)$$

Setting the derivatives of Equation 6 with respect to $\overline{\Delta}a$, $\overline{\Delta}b$, and $\overline{\Delta}d$ equal to zero, the condition for a minimum in E^2, gives three equations which may be solved for the three unknowns. The heat capacity of a metal salt may then be estimated by adding Equation 7 to the equation for the metal oxide heat capacity.

$$\overline{\Delta} = \overline{\Delta}a + \overline{\Delta}b\ T - \overline{\Delta}d/T^2 \qquad (7)$$

Dividing Equation 6 by the sum of the temperature ranges of validity for the J oxide-salt combinations and taking the square root gives the RMS error. The accuracy was expressed as the fractional error, or the RMS error divided by the average known heat capacity for the group of compounds of interest. Tables I, II, and III show the errors for carbonates, sulfates, and sulfides, respectively.

TABLE I

ESTIMATED HEAT CAPACITIES FOR CARBONATES WITH KNOWN HEAT CAPACITIES
CAL./ GMOLE/ DEG.KELVIN
CP = CP(OXIDE) + DELTA CP

DELTA CP = 1.3056+01 + 5.8660-03*T - 5.7699+05/T**2

	METAL CARBONATE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE	FRACTIONAL RMS ERROR
1	AG2CO3	2.630568+01	1.290403-02	5.769911+05	2.500+01 TO 7.000+02	6.086-02
2	BACO3	2.578883+01	6.905248-03	7.752781+05	2.500+01 TO 7.000+02	3.927-02
3	CACO3	2.491211+01	6.945861-03	7.430256+05	2.270+02 TO 6.270+02	3.505-02
4	FECO3	2.471144+01	7.865626-03	6.529613+05	2.500+01 TO 1.200+03	4.737-02
5	MGCO3	2.323026+01	7.605225-03	7.248702+05	2.500+01 TO 1.727+03	1.045-02
6	MNCO3	2.415958+01	7.605901-03	6.649063+05	2.500+01 TO 1.200+03	2.378-02
7	NA2CO3	2.874885+01	1.126278-02	5.769911+05	2.500+01 TO 7.000+02	1.182-01
8	SRCO3	2.533991+01	6.986474-03	7.575995+05	2.500+01 TO 7.000+02	6.719-02

TABLE II

ESTIMATED HEAT CAPACITIES FOR METAL SULFATES WITH KNOWN HEAT CAPACITIES
CAL./ GMOLE/ DEG.KELVIN
CP = CP(OXIDE) + DELTA CP

DELTA CP = 9.0132+00 + 1.6828-02*T - -4.6680+04/T**2

	METAL SULFATE	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE	FRACTIONAL RMS ERROR
1	AG2SO4	2.226737+01	2.386632-02	-4.668011+04	2.500+01 TO 7.000+02	8.104-02
2	AL2(SO4)3	5.344459+01	5.482499-02	6.522597+05	2.500+01 TO 7.000+02	1.626-02
3	BASO4	2.174657+01	1.786755-02	1.516069+05	2.500+01 TO 7.000+02	8.648-02
4	BESO4	1.745831+01	2.082752-02	2.701013+05	2.500+01 TO 7.000+02	6.482-02
5	CASO4	2.085980+01	1.790816-02	1.193554+05	2.270+02 TO 6.270+02	2.111-02
6	CDSO4	1.865998+01	1.890676-02	-4.668011+04	2.500+01 TO 7.000+02	2.016-02
7	CUSO4	1.828013+01	2.162544-02	-4.668011+04	2.500+01 TO 7.000+02	8.156-02
8	MGSO4	1.918795+01	1.856752-02	1.011990+05	2.500+01 TO 1.727+03	2.573-02
9	MNSO4	2.011727+01	1.876820-02	4.123509+04	2.500+01 TO 1.200+03	3.120-02
10	NA2SO4	2.470654+01	2.222508-02	-4.668011+04	2.500+01 TO 7.000+02	6.424-02
11	PBSO4	1.960841+01	2.082752-02	-4.668011+04	2.500+01 TO 6.000+02	4.856-02
12	SRSO4	2.134760+01	1.794877-02	1.339283+05	2.500+01 TO 7.000+02	7.098-02
13	ZNSO4	2.071691+01	1.804672-02	1.711967+05	2.500+01 TO 1.200+03	4.332-02

TABLE III

ESTIMATED HEAT CAPACITIES FOR METAL SULFIDES WITH KNOWN HEAT CAPACITIES
CAL./ GMOLE/ DEG.KELVIN
CP = CP(OXIDE) + DELTA CP

DELTA CP = 1.7972+00 + -1.0570-03*T - -1.6525+04/T**2

	METAL SULFIDES	A	B	D	TEMPERATURE RANGE DEGREES CENTIGRADE	FRACTIONAL RM ERROR
1	AG2S	1.305138+01	5.980967-03	-1.652523+04	2.500+01 TO 7.000+02	1.296-01
2	BI2S3	3.011778+01	4.824901-03	-4.957569+04	2.500+01 TO 5.000+02	8.404-03
3	CDS	1.144399+01	1.021403-03	-1.652523+04	2.500+01 TO 7.000+02	9.865-02
4	FES	1.345314+01	9.425657-04	5.944497+04	2.500+01 TO 1.200+03	1.060-01
5	MGS	1.197196+01	6.821647-04	1.313539+05	2.500+01 TO 1.727+03	1.045-01
6	MNS	1.290123+01	8.828407-04	7.138997+04	2.500+01 TO 1.200+03	4.364-02
7	NA2S	1.749055+01	4.339724-03	-1.652523+04	2.500+01 TO 7.000+02	2.380-03
8	PBS	1.239242+01	2.942159-03	-1.652523+04	2.500+01 TO 6.000+02	9.568-02
9	SB2S3	2.447974+01	1.351027-02	-4.957569+04	2.500+01 TO 9.000+02	9.250-03
10	SNS	1.134365+01	2.440469-03	-1.652523+04	2.500+01 TO 7.000+02	5.009-02
11	SNS2	2.124674+01	2.845014-04	4.827346+05	2.500+01 TO 1.200+03	4.677-02
12	TIS2	2.072594+01	-1.134565-03	3.166991+05	2.500+01 TO 1.200+03	2.217-02
13	US2	2.273525+01	-4.943126-04	3.625679+05	2.500+01 TO 1.200+03	3.686-02
14	ZNS	1.350092+01	1.613627-04	2.013516+05	2.500+01 TO 1.200+03	3.062-02

Copy made for Chemistry Files

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

1 May 1968

K. Schwitzgebel
P. Lowell

TECHNICAL MEMORANDUM 004-009-Ch 2

ESTIMATION OF UNCERTAINTIES CAUSED BY ERRORS IN HEAT OF REACTION AND ABSOLUTE ENTROPIES

The equilibrium partial pressures of gases over solids is important in the SO_2 sorption problem.

It is of interest to know the uncertainties in equilibrium partial pressures caused by errors in experimental and estimated values of heat of formation and absolute entropy. The partial pressure of SO_2 in the equilibrium system SO_2 - metal oxide - metal sulfite will be used as an example.

For the formation or decomposition of sulfites the dependency of decomposition pressure on temperature is of interest. The decomposition pressure is given by the relation

$$\ln(p_{SO_2}) = \ln K_p = - \frac{\Delta G}{RT} = - \frac{1}{R} \left(\frac{\Delta H}{T} - \Delta S\right)$$

The error ΔH_u in the heat of reaction ΔH, and the error ΔS_u of the entropy of reaction ΔS will cause errors in the final results.

After calculating and plotting the expected log K as a function of temperature, there are two questions of importance:

Case 1: What is the uncertainty Δ log K for a fixed temperature?
Case 2: What is the uncertainty ΔT_u in temperature for a fixed log K?

The uncertainty may be estimated by assuming the error propagation is Gaussian. The following symbols are defined:

ΔH_u = error in the heat of reaction ΔH

ΔS_u = error in the entropy of reaction ΔS

ΔT_u = error in the temperature T, when log K is fixed

Δ log K = error in log K, when T is fixed

Starting from the basic equation

$$\log K = - \frac{\Delta G}{2.303\ RT} = - \frac{1}{2.303\ R} \left(\frac{\Delta H}{T} - \Delta S\right) \qquad (1)$$

Case 1: Uncertainty Δ log K for a fixed temperature.

The uncertainty Δ log K is given by the equation

$$\Delta \log K = \pm \left[\left(\frac{\partial \log K}{\partial \Delta S}\right)^2 \cdot \Delta S_u^2 + \left(\frac{\partial \log K}{\partial \Delta H}\right)^2 \Delta H_u^2\right]^{1/2} \qquad (2)$$

$$\Delta \log K = \pm \frac{1}{2.303\ RT} \left[T^2\ \Delta S_u^2 + \Delta H_u^2\right]^{1/2}$$

Example 1: The average deviation of the estimated heat of formation of the sulfites is of the order of magnitude of 2 kcal/mole. Assume therefore that at 298°K the error in the heat of reaction is about 3 kcal/mole. Comparing estimated and measured entropies one may assume that at 298°K the entropy of reaction has an error of about 2 cal/mole °K. With these values Δ log K is given at 298°K by

$$\Delta\log K \approx \pm \frac{1}{(4.6)(300)} \left[0.36 \times 10^6 + 9 \times 10^6\right]^{1/2}$$

$$\Delta \log K \approx \pm 2.2$$

At room temperature the uncertainty in log K caused by an error in ΔS is negligible compared to the uncertainty caused by an error in ΔH.

Example 2: At temperatures other than 298°K the errors in ΔH_T and ΔS_T have additional uncertainties because of the errors in the $\Delta Cp(T)$ function. These will be neglected at this time.

With the same values for ΔH_u and ΔS_u as in Example 1 it can be seen for T = 1000°K

$$\Delta \log K \approx \frac{1}{4.6 \times 1000} \left[4 \times 10^6 + 9 \times 10^6\right]^{1/2}$$

$$\Delta \log K \approx \pm 0.8$$

The uncertainty in log K due to the uncertainties in $\Delta H_{298}°$ and $\Delta S_{298}°$ becomes smaller at the higher temperatures.

Case 2: Uncertainty ΔT_u of T for a fixed log K.

Equation (1) may be expressed in a temperature explicit form.

$$T = \frac{\Delta H}{\Delta S - 2.303\ R \times \log K} \tag{3}$$

The error in T is given by:

$$\Delta T_u = \pm\left[\left(\frac{\partial T}{\partial \Delta H}\right)^2 \Delta H_u^2 + \left(\frac{\partial T}{\partial \Delta S}\right)^2 \Delta S^2{}_u\right]^{1/2} \qquad (4)$$

$$\Delta T_u = \pm\frac{T}{\Delta H}\left[\Delta H^2{}_u + T^2 \Delta S^2{}_u\right]^{1/2} \qquad (5)$$

Again assume $\Delta H_u = \pm 3$ kcal and $\Delta S_u = \pm 2$ cal/mole °K. For the decomposition of the sulfites, the heat of reaction, ΔH_{298} , is about + 50 kcal/mole (For $Li_2SO_3 = +66.0$; for $Na_2SO_3 = +86.6$; for $CdSO_3 = +31.8$ and for $PbSO_3 = +33.7$ kcal/mole).

Example 1: T = 298°K

$$\Delta T_u \approx \pm \frac{298}{50 \times 10^3}\left[9 \times 10^6 + 0.36 \times 10^6\right]^{1/2}$$

$$\Delta T_u \approx \pm 18°K$$

Example 2:

$T = 1000°K$; $\Delta H = +50$ kcal/mole, $\Delta H_u = 3$ kcal/mole, $\Delta S_u = 2$ cal/mole °K

$$\Delta T_u = \pm \frac{10^3}{5 \times 10^4}\left[9 \times 10^6 + 4 \times 10^6\right]^{1/2}$$

$$\Delta T_u \approx \pm 72°K$$

It can be seen that with fixed log K, the uncertainty in T is greater at higher temperatures.

TRACOR 6500 TRACOR LANE AUSTIN, TEXAS 78721

29 January 1969

T. Parsons
K. Schwitzgebel

TECHNICAL MEMORANDUM 004-009-Ch18

CONFLICTING AND ACCEPTED VALUES FOR THERMODYNAMIC PROPERTIES

I. INTRODUCTION

In preparing the TRACOR compilation of thermodynamic properties, the following major compilations were consulted.

1. Landolt Boernstein, Kalorische Zustandsgrössen (1961). This compilation is based on a review of all thermodynamic data published up to 1960.
2. Selected Values of Thermodynamic Properties, the National Bureau of Standards, Circular 500, (1952), and the Technical Notes NB-270-1, NB-270-2, NB-270-3.
3. JANAF, Thermochemical Tables and Supplements. This compilation is limited to only part of the elements.
4. Metallurgical Thermochemistry, Kubaschewski, Evans, and Alcock, 4th. Edition, 1967.

In addition to these compilations, values published in the open literature have been included using Chemical Abstracts as a guide. The review covers the period from 1960 through 1967.

It is recognized that compilations may differ slightly due to internal consistency. There is no doubt that all of the authors used extreme care in preparing their tables. Nevertheless in some cases the reported values for a particular compound differed significantly. In these cases, the original literature from which these values were taken was reviewed.

The following criteria have been used in selecting the value used in the TRACOR data base for the heat of formation.

1. Calorimetric measurements have generally been preferred. These measurements are usually the most straightforward. The experiments are normally performed at room temperature or slightly elevated temperatures. On the other hand, EMF or vapor pressure measurements are usually carried out at fairly high temperatures, often at temperatures above 800° C. In order to arrive at standard values, the measured data must be recalculated over a large temperature difference using heat capacity equations. When measured heat capacities were unavailable, the authors often used estimated values. Another difficulty with EMF or vapor pressure measurements lies in the fact that the phases present must be well defined. Table I shows that conflicting values may be the result of disregarding this fact.

2. In some cases calorimetrically determined values are based on multi-step thermodynamic cycles according to Hess' Law. For instance, the data for the alkaline earth and alkali metal sulfides were derived from the solution calorimetry data of Sabatier (SA-001) published in 1881. The values published by Sabatier have been subsequently revised when one of the thermodynamic quantities in his cycle was redetermined. In spite of

these revisions, the values published in the compilations still differ. For the alkali metal sulfides, we based our selection on the fact that the change in thermal properties for the elements of a particular periodic sub-group is gradual and regular provided the compounds have the same crystal lattice. This criteria is fulfilled by the alkali metal sulfides which have the CaF_2 structure.

3. In general, we have preferred values for which the limits of accuracy were described by the authors.

The criteria used in the selection of conflicting entropy values were similar.

1. Entropy values derived from low temperature heat capacity measurements were preferred over those based on high temperature EMF and vapor pressure measurements. In the first place, they are more straightforward; and in the second place, they are independent of high temperature heat capacities.

2. Values for which an error estimation was made were preferred.

The selected heats of formation are contained in Table I, and the selected entropy values in Table II. When one reference follows another in parentheses, the second reference was cited by the first author as the basis for his data.

The decisions were not always clear, even when the above criteria were applied.

Terry B. Parsons

TABLE I

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
Al_2S_3	-172.85 ± 4.3 -172.9 ± 4.0 -121.6	LA-001 (KA-001) KU-001 (KA-001) NB-003 (KO-001)	The values cited for the heat of formation of aluminum sulfide differ by 50 kcal. The values chosen by Landolt Boernstein (LA-001)and Kubaschewski (KU-001) were the same and were based on the same data (KA-001). The value cited in NBS Circular 500 (NB-003) was designated as unreliable by by Kubaschewski in his 1967 compilation (KU-001). Kubaschewski's claim was not investigated. The original literature was in Russian (1939 and 1951) and was not translated into English.	-172.9: 1) Landolt Boernstein and Kubaschewski agree. 2) This was the most recently determined value. 3) Kubaschewski criticized the earlier determined value.
As_2S_3	-34.87 -30.0 ± 3.0	LA-001 (KU-004) KU-001 (No Ref.)	Landolt Boernstein based his value on Kubaschewski's publication of 1943. In the 1967 edition of Kubaschewski's book, the value was revised. The author, however, gave no reason for the revision.	-30.0
BaS	-110.8 -106.0 -106.0 -106.0 ± 5.0	LA-001 (RO-006) NB-003 (SA-001) CA-019 (SA-001) KU-001 (NB-003)	Rossini and Bichowsky (RO-006) based their value on the 1881 publication of Sabatier (SA-001). Sabatier determined the heat of solution of several sulfides in HCl. The results were used as part of a six-step thermodynamic Hess' Law summation. The other four unknowns were taken from a publication by Berthelot (BE-002). The value of Kubaschewski was taken as the accepted one; his limits of validity include the value of Landolt Boernstein.	-106.0
B_2O_3 (c)	-302.0 ± 3.4 -306.1 ± 4.5	LA-001 (JO-001) KU-001 (NB-003, BR-001)	The value for the heat of formation of crystalline B_2O_3 was reported by Landolt Boernstein (LA-001) as -302.0 ± 3.4 kcal. It was taken directly from the 1951 work of Johnston (JO-001) who calculated the value from the heats of the following reactions: $2B\ (amorphous) + 3H_2(g) \rightarrow B_2H_6(g)$ (1) $B_2H_6(g) + 6H_2O(\ell) \rightarrow 2H_3BO_3(aq) + 6H_2(g)$ (2) $2H_3BO_3(aq) \rightarrow B_2O_3(c) + 3H_2O(\ell)$ (3) $3H_2(g) + {}^3/_2O_2(g) \rightarrow 3H_2O(\ell)$ (4) $2B(c) \rightarrow 2B\ (amorphous)$ (5) $2B(c) + {}^3/_2O_2 \rightarrow B_2O_3(c)$ (6) The value for heat of formation reported by Kubaschewski (KU-001) was taken from the 1953 review by Brewer (BR-001). Kubaschewski reported -306.1 kcal (KU-001) but in the original review it was actually reported as:	-306.1

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
B_2O_3 (c) (continued)			$\frac{1}{3}\Delta H_f^\circ = -101.8 \pm 1$ or $\Delta H_f^\circ = -305.4 \pm 3$ kcal. Brewer stated that his value was based on private communications to the National Bureau of Standards concerning the heat of hydrolysis of diborane, which is represented by Equation 2 in the reaction scheme. Apparently Kubaschewski made further recalculations based on more recent data. He did not mention in his 1967 edition which value in the cycle was changed.	
$CaFe_2O_4$	-397.75	LA-001 (MA-005)	Landolt Boernstein's value was based on the 1926 publication of Marchal (MA-005). Marchal found a value of -49.6 kcal for the heat of formation from the oxides which seems inordinately high when compared with -9.2 kcal for $MgFe_2O_4$ and -22 kcal for $BaFe_2O_4$. The journal cited in Chemical Abstracts (CA-042) did not contain the Russian article in question. Therefore, we could not read the original literature. The value for the heat of reaction for: $CaO + Fe_2O_3 \rightarrow CaFe_2O_4$ (7) determined using solution calorimetry was given in the abstract as -19.1 kcal/mole. With this value and the heats of formation from the TRACOR data base, we calculated the heat of formation as -367.25kcal which is 8 kcal different from the TRACOR estimate (TR-002).	-367.25: Landolt Boernstein's value was unreasonably high.
	-367.25	CA-042		
	-359.2	TR-002		
$CaMoO_4$	-367.3 ± 0.9	HE-003	The value of Muldrow and Hepler (HE-003) was determined from heat of precipitation measurements. Rezukhina and co-workers (CA-021) stated in their original article that the value may be too low due to formation of polymolybdates. Rezukhina and co-workers redetermined the value using EMF methods. From their data they calculated the free energy change for the following reactions from 1252 to 1366°K. $CaMoO_3 + \frac{1}{2}O_2 \rightarrow CaMoO_4$ (8) $CaO + Mo + O_2 \rightarrow CaMoO_3$ (9) In order to calculate standard values, it was assumed that the heat capacity of $CaMoO_3$ was equal to that of $CaTiO_3$ and that the heat capacity of $CaMoO_4$ was equal to the average of the heat capacities of $SrMoO_4$ and $MgMoO_4$.	-369.2: Solution calorimetry seems to be the most straightforward method.
	-369.2 ± 0.1	KU-001 (CA-077)		
	-372.3 ± 5.2	CA-021		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
$CaMoO_4$ (continued)			The value reported by Kubaschewski was based on the U.S. Bureau of Mines work of 1962 (CA-077). The heat of formation from the oxides was determined using solution calorimetry. The pure oxides and and $CaMoO_4$ were dissolved in a mixture of concentrated sulfuric and phosphoric acids at 150° C. The difference in the heats of solution is equal to the heat of reaction at this temperature.	
CaS	-110.0 ± 2.5 -115.3 -114.2	KU-001 (No Ref.) NB-003 (WA-001) LA-001 (WA-001)	Kubaschewski gave no reference for his value. The data of the National Bureau of Standards and Landolt Boernstein are both based on the work of von Wartenberg (WA-001). Von Wartenberg determined the heats of the following reactions: $CaS + 2HCl, 30H_2O \rightarrow CaCl_2 + H_2S$ ($\Delta H = -20.6 \pm 0.2$kcal) (10) $Ca + 2HCl, 30H_2O \rightarrow CaCl_2 + H_2$ ($\Delta H = -129.9 \pm 0.5$kcal) (11) By subtraction of these equations the heat of the reaction in Equation 12: $Ca + H_2S \rightarrow CaS + H_2$ (12) was found to be -109.3 ± 0.54 kcal/mole. From this value and the heat of formation of H_2S given by Kubaschewski (-4.9 kcal), we calculated the heat of formation of CaS to be -114.2 kcal. The value of Landolt Boernstein was therefore accepted.	-114.2
$CaWO_4$	-392.5 -402.5 ± 0.35 -394.8 -397.8	CA-025 KU-001 (CA-077) LE-003 LE-003	The value reported by Kubaschewski was based on the work of the U.S. Bureau of Mines (1962)(CA-077). The value was calculated from the measured heats of the following reactions. $CaO + 2HF \rightarrow CaF_2 + H_2O(\ell)$ (13) ΔH $NaWO_4 \rightarrow 2Na^+ + WO_4^=$ (14) $2HCl \cdot XH_2O \rightarrow 2H^+ + 2Cl^- + XH_2O(sol.)$ (15) $2NaCl \rightarrow 2Na^+ + 2Cl^-$ (16) ΔH $XH_2O(\ell) \rightarrow XH_2O(sol.)$ (17) $CaWO_4 + 2HF \rightarrow CaF_2 + 2H^+ + WO_4^=$ (18) By subtraction: $CaO + Na_2WO_4 + 2HCl \cdot XH_2O \rightarrow 2NaCl + H_2O + CaWO_4$ (19) $\Delta H = \Delta H - \Delta H = -53.44 \pm 0.14$ kcal/mole	-402.5: This value was accepted because it was the only one for which the error estimations were available. The method does not appear to be straightforward, however, calorimetric methods have been generally considered more reliable than EMF or equilibrium measurements.

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
$CaWO_4$ (continued)			This value was combined with published values for the heats of the following reactions: $H_2WO_4 + H_2O + 2NaCl \rightarrow Na_2WO_4 + 2HCl \cdot XH_2O$ (20) $WO_3 + H_2O \rightarrow H_2WO_4$ (21) For the reaction: $CaO + WO_3 \rightarrow CaWO_4$ (22) the heat was then determined to be -49.16 ± 0.35 kcal. The heat of formation of $CaWO_4$ is therefore -402.5 kcal/mole. The value reported by Levitskii and co-workers (CA-025) was also determined by calorimetry; however, no error estimation was given in the abstract. The original article [Izv. Akad. Nauk SSSR, Neorgan. Materialy, Vol. 2, p. 325-31 (1966)] could not be located on the University of Texas Campus. The same authors previously published two values for the heat of formation of $CaWO_4$. One was obtained by EMF measurements (-394.8 kcal/mole) and the other from hydrogen reduction equilibria (-397.8 kcal/mole) (LE-003). Error estimations were not given for the values.	
CoS	-22.7	LA-001 (SU-001)	The heat of formation of cobalt sulfide has been reported in values ranging from -18.6 (CA-071) to -22.7 (LA-001) kcal. The value published by the National Bureau of Standards (NB-003), -20.2 kcal, was based on the equilibrium pressure data of Jellinek and Zakowskii (JE-001), and Landolt Boernstein's value (LA-001) was based on similar measurements by Sudo (SU-001). T. Rosenqvist (RO-004), who studied the equilibria of cobalt, iron, and nickel sulfides with hydrogen from 600 to 1200°C, clearly defined the metal-sulfide phase compositions at different temperatures and discussed at length the problems, such as thermal diffusion errors and the presence of variety of sulfide phases, involved in measuring H_2S/H_2 partial pressures at equilibrium. Rosenqvist used special experimental techniques to circumvent the problems of thermal diffusion. In his discussion of the cobalt-sulfur system, he stated that both Jellinek and Zakowskii (JE-001) and Sudo (SU-001) neglected to define the composition of the sulfides present at equilibrium. They assumed the presence of CoS and Co. In the temperature range for which their measurements were made, however, Rosenqvist pointed out that lower sulfides are also stable.	-21.07
	-20.2	NB-003 (JE-001)		
	-18.6	CA-071		
	-21.07	RO-004		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
CoS (continued)			E. M. Kolbina (CA-071) also carried out equilibrium partial pressure measurements on H_2S/H_2 as a function of sulfide composition between 785 and 845°C. His data gave a value of -18.6 kcal for the heat of formation of CoS.	
$CoSO_4$	-207.3 -207.5 ± 6.0 -211.9 ± 0.4	LA-001 (NB-003) KU-001 (NB-003) AD-001 NB-003 (KE-005)	The values given by Landolt Boernstein and Kubaschewski were based on vapor pressure measurements of the U.S. Bureau of Mines determined in 1937 (KE-005). Calculation of the heat of formation from these data included estimated heat capacity and entropy values. In 1965 the U.S. Bureau of Mines (AD-001) redetermined the thermodynamic properties of $CoSO_4$ using solution calorimetry. The value depends on the heat of formation of CoO as found in the TRACOR data base and on the heat capacities of Co and $CoSO_4$ from Kelley's U.S. Bureau of Mines publication Bulletin 592 (1961). The value determined by solution calorimetry (AD-001) is the accepted one.	-211.9
$FeCr_2O_4$	-349.5 ± 1.0 -337.64 ± 2.5 -341.63	CA-068 KU-001 (No Ref.) LA-001 (BO-002)	The value published by Landolt Boernstein was based on the 1945 data of Boericke and Bangert (BO-002). They carried out equilibrium measurements for the following reaction: $FeO \cdot Cr_2O_3 + H_2 \rightarrow Fe + Cr_2O_3 + H_2O(g)$ (23) Their evaluation of the equilibrium measurements depended on the heat of formation of Cr_2O_3 which they took to be -269.7 kcal/mole instead of the accepted value of -272.7 kcal/mole. Evaluation of the value published by Kubaschewski was impossible since he gave no reference. The value of the Russian authors Levitskii and Rezukhina (CA-068) was determined using EMF measurements and agreed within 1.4 kcal with the free energies calculated from the data of Morozova and Novokhatskii (MO-002) and Chan and Chipman (CH-002).	-349.5
$FeTiO_3$	-288.34 (-295.1 ± 1.2) -299.7 ± 1.4 -294.17	LA-001 (SH-002) CA-031 TR-002	Lenev and Novokhatskii (CA-031) studied the reduction equilibrium of $FeTiO_3$ and CO at 1000°C. They obtained a value of -10.4 ± 0.5 for the heat of the following reaction: $FeO + TiO_2 \rightarrow FeTiO_3$ (24) This yielded a value of -299.7 ± 1.4 kcal/mole for the heat of formation of $FeTiO_3$ using the values for heat of formation from the TRACOR data base.	-295.1: It was not possible to decide which value was the most accurate. The value of -295.1 was chosen because it is close to the TRACOR prediction.

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
$FeTiO_3$ (continued)			The value published by Landolt Boernstein was based on the data of Shomate, Naylor, and Boericke (SH-002) who determined in 1946 the following thermodynamic properties of iron metatitanate: 1) low temperature specific heats up to 298.16°K for standard entropy calculations; 2) high temperature heat contents; 3) hydrogen reduction equilibria according to the reaction: $FeTiO_3 + H_2 \rightarrow Fe(\gamma) + TiO_2(\text{rutile}) + H_2O(g) \quad (25)$ From these measurements the heat of the following reaction was determined as -6.28 ± 0.4 kcal. $FeO + TiO_2 \rightarrow FeTiO_3 \quad (26)$ The heat of formation of $FeTiO_3$ was then calculated using a value of -220.0 kcal for TiO_2 while the accepted value is -225.5 kcal. Using the latter, the heat can be recalculated as -295.1 ± 1.2 kcal/mole. The value estimated by the TRACOR correlation (TR-002) falls within the range of this value.	
Ga_2O_3	(-433.88)	LA-001 (HU-008)	The heat of formation of gallium sesquioxide appeared at first to be a matter of some contention since the value reported by Landolt Boernstein (LA-001) differed by more than 200 kcal from that reported in the other compilations (KU-001, NB-002). Landolt Boernstein gave the work of Huber and Holley (HU-008) as a reference. Huber and Holley do report a heat of formation of -433.8 kcal, but the value was determined for gadolinium, not gallium. Kubaschewski's value of -258.8 kcal was based on Brewer's review (BR-001). It was reported there as: $\frac{1}{3}\Delta H_f^\circ = -86 \pm 1 \quad \text{or} \quad \Delta H_f^\circ = -258 \pm 3 \text{ kcal}$ Brewer obtained his value from the combustion measurements of Klemm and Schnick (KL-001), who measured the heat of combustion of gallium and obtained -260 and -258 ± 1 kcal. The accepted value will be that reported by A. D. Mah of the U.S. Bureau of Mines (MA-003). Mah determined the heat of combustion of pure liquid gallium to β-Ga_2O_3 and calculated the heat of formation of the oxide using the heat of fusion of gallium. Her value was -261.05 ± 0.3 kcal. The National Bureau of Standards (NB-002) reported a value of -263.7 kcal with no reference given. That value was the value found by Mah for the heat of reaction in Equation 27, before she added the heat of fusion for two moles of gallium (+ 2.67 ± 0.1 kcal).	-261.05
	-258.8 ± 1.2	KU-001 (BR-001, KL-001)		
	-261.05 ± 0.3	MA-003		
	-263.7	NB-002		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
Ga_2O_3 (continued)			$2Ga(\ell) + {}^3/_2 O_2(g) \rightarrow Ga_2O_3(\beta)$ (27)	
GeS	-16.5	NB-005	Landolt Boernstein took the data of Barrow and Dodsworth (BA-001) who determined the vapor pressure of germanous sulfide. Barrow and Dodsworth reported a temperature error of 6-7°C and used a heat capacity estimated from Kelley's stannous and lead sulfide heat capacity data plus a heat of sublimation for GeS of ± 4 kcal accuracy. The resulting uncertainty in their heat of formation value is ± 8.5 kcal. The value for heat of formation given by Kubachewski (KU-001) was taken from the paper by C. Hirayama (HI-001) who compiled the thermodynamic properties of the chalcogenides (S, Se, Te, O compounds) of lead, tin, and germanium. Hirayama used GeS vapor pressure measurements of five different workers including those of Barrow and Dodsworth (BA-001) to recalculate the heat of formation of GeS as 21.4 ± 2 kcal. The uncertainty was due to the uncertainty in heat of sublimitation of GeS. The value reported by Kubaschewski will be the accepted one. The National Bureau of Standards Technical Note 270-3 (NB-005) gave a value of -16.5 kcal for germanium sulfide. Since no reference is given it is impossible to evaluate this datum.	-21.4
	-25.8 ± 8.5	LA-001 (BA-001)		
	-21.4 ± 2	KU-001 (HI-001)		
HfO_2	-266.1 ± .3	LA-001 (HU-007)	The heat of formation of hafnium dioxide was reported by Landolt Boernstein (LA-001) and the National Bureau of Standards (NB-003) and later redetermined by Huber and Holley (HU-006). The value determined by Huber and Holley, -273.6 kcal, will be the accepted one. The authors commented on the work on which the previously published values were based (RO-003, HU-007). One of the combustion experiments was carried out with hafnium metal containing 2.4% zirconium. In one case there were only two determinations carried out, the results were greatly differing, and 80% of the energy of combustion was contributed by sources other than the burning of hafnium. In neither case was the sample analyzed for oxygen content. Huber and Holley's heat of combustion determinations were carried out 13 times with a standard deviation of 0.8 cal from the mean value.	-273.6
	-271.5	NB-003 (RO-003)		
	-273.6	HU-006		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
IrO_2	-44.0 ± 6	BR-001 (WO-001, WO-002)	The value cited by Landolt Boernstein was taken from Brewer's review (BR-001). Brewer reported the two values determined earlier (1908, 1933) by Wöhler. 1) Using vapor pressure measurements Wöhler calculated ΔH_f = -50 kcal (WO-001). 2) Using calorimetric measurement of the heat of the reaction in Equation 28: $IrO_2 + 2H_2 \rightarrow Ir + 2H_2O$ (28) Wöhler calculated ΔH_f° = -40.2 kcal (WO-002). Brewer calculated a weighted average of the two values and reported -44 kcal. The value cited by Kubaschewski was based on the work of Schaefer and Heitland (SC-001). Schaefer and Heitland based their value on dynamic equilibrium measurements for the $Ir + 1.5\ O_2 \rightarrow IrO_3(g)$ (29) $IrO_2(c) + 0.5\ O_2 \rightarrow IrO_3(g)$ (30) by subtraction: $Ir + O_2 \rightarrow IrO_2(c)$ (31) From this reaction they derived a value of -53.5 kcal/mole which agreed well with the value obtained from decomposition measurements of IrO_3 (-52.4 kcal/mole). The gas streaming rate was about 33-100 ml/min. The lower limit was therefore the same as that reported by Meyer and Cordfunke. The value reported by Meyer and Cordfunke (ME-001) was based on two series of measurements. One was the determination of oxygen pressure over an IrO_2-Ir mixture to define the composition of the resulting non-stoichiometric oxide. For the reaction: $IrO_2 \rightleftharpoons IrO_{2-x} + \frac{x}{2} O_2$ (32) they plotted log p_{O_2} vs. 1/T and obtained for the enthalpy of formation of IrO_2: ΔH_{1230° = -58.1 kcal In the second experiment (ME-003), the authors carried out dynamic partial pressure measurements (streaming rate 35 ml/min) over Ir and IrO_2 and obtained heats for the following reactions:	-53.0
	-44.0 ± 6	LA-001 (BR-001)		
	-53.0 ± 2.5	KU-001 (SC-001)		
	-65.5 ± 1.5	ME-001		
	-40.14	WO-002		
	-50.0	WO-001		

TABLE I (continued)
CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
IrO_2 (continued)			$Ir + 1.5O_2 \rightarrow IrO_3 \quad \Delta H_{1580°K} = 4.65$ kcal (33) $2IrO_2(s) + O_2 \rightarrow 2IrO_3(g) \quad \Delta H_{1320°K} = 63.13$ kcal (34) They calculated $\Delta H^F_{1550°K}$ for IrO_2 by assuming the two ΔH values constant over 100°. This resulted in $\Delta H^F_{1550°K}$ for IrO_2 = -58.5 kcal. Using Kelley's heat capacity values (KE-008), they reduced these values to 298.16° K and obtained -64.0 (ME-001) and -67.1 (ME-003). They reported a value of -65.5 ± 1.5 kcal. The value of Schaefer and Heitland is the accepted one since it is close to the average of all the values. No other criteria were applicable.	
IrS_2	-30.0	NB-003 (BI-003)	The heat of formation of iridium disulfide was published by the National Bureau of Standards (NB-003) as -30 kcal. Their value was based on the isothermal decomposition pressure data of Biltz and Laar (BI-003). The calculations of Biltz and Laar were apparently made with the assumption that the heats of formation at 1050 and 25° C were identical. L. G. Hepler, in his review of the platinum metals (HE-002), recalculated the heat of formation using Biltz' data and the heat capacity reported by Westrum (WE-001). Hepler obtained the value -34 kcal which will be the accepted value for the TRACOR data base.	-34.0
	-34.0	HE-002 (BI-003, WE-001)		
Ir_2S_3	-42.0 ± 7.9	LA-001 (KU-002, BI-003)	The data of Landolt Boernstein (LA-001) and National Bureau of Standards (NB-003) for the heat of formation of Ir_2S_3 were both based on the dissociation pressures of Biltz and Laar (BI-003). Kubaschewski gave his Thermochemie der Legierungen (KU-004), published in 1943, as a reference. We were unable to locate a copy to investigate the basis for his data. Hepler's recent review (HE-002) again gave a value for the heat of formation recalculated from the Biltz data with Westrum's heat capacity (WE-001) (See IrS_2). This value was accepted because it was a re-evaluation of the earlier measurements using new heat capacity data.	-58.0
	-42.0 ± 6.0	KU-001 (KU-004)		
	-51.0	NB-003 (BI-003)		
	-58.0	HE-002 (BI-003, WE-001)		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
K_2S	-87.86 -100.0 -102.4 ± 3.5 -102.6 to -104.2	LA-001 (BR-004) NB-003 (RE-003) KU-001 (NB-003) SA-001	The heat of formation of potassium sulfide was reported by Landolt Boernstein (LA-001) with an original reference (BR-004) which we were unable to locate. The value, -87.86, differs by about 13 kcal from the values reported by the National Bureau of Standards (NB-003) and Kubaschewski (KU-001). Kubaschewski gave NBS as a reference and NBS gave the early heat of solution measurements of Renegade and Consteanu (RE-003) as a basis for their data. The value chosen by Kubachewski was near the value published by Sabatier (SA-001).	-87.86: The heats of formation of the alkali metal oxides and sulfides are as follows: Element / Oxide / Sulfide Li / -142.5 / -107.4 Na / -102.87 / - 92.4 K / - 86.36 / Rb / - 79. / - 83.2 Cs / - 76. / - 81.1 The sulfides of lithium, sodium, potassium, and rubidium are cubic and have the CaF_2 type crystal structure (KU-001) From these facts and the recognized trends for elements in the same periodic group, it appears as if the value -87.86 is the most reasonable one.
La_2O_3	-538.0 @ 22° C -458.0 ± 9 -428.57 ± 0.9 -430.5 ± 1 -433.5 ± 4 -447.0 to -457.0	LA-001 (RO-001) NB-003 (RO-001) HU-001 KU-001 (BR-001) BR-001 RO-001	For lanthanum sesquioxide, the heat of formation value of -430.5 ± 1 kcal cited by Kubaschewski (KU-001) was chosen as the most reliable. Both Landolt Boernstein and the National Bureau of Standards cited the same reference (RO-001) although the values they quoted were quite different. The experimental procedure used by Roth (RO-001) was combustion calorimetry. The authors reported that they used a pure metal, but no analysis was given. According to Brewer impurities present cause heat of combustion results that are too high. The authors also reported difficulties due to sublimation and sintering of the oxide. Kubaschewski (KU-001) referenced L. Brewer's review on metal oxides (BR-001). Brewer gave -433.5 ± 1 kcal from his own heat of combustion measurements. The values given by Huber and Holley (HU-001) and Brewer were within the range of that value cited by Kubaschewski, which was essentially the average of the two values.	-430.5
LaS_2	-156.7 -145.0 ± 7	NB-003 (BI-002) KU-001 (NB-003)	The values for the heats of formation of the lanthanum sulfides LaS_2 and La_2S_3 were ultimately based on the work of Biltz (BI-002). Biltz measured the heat of solution of LaS_2 and La_2S_3 in HCl. From the values obtained, he gave the heat of the reaction in Equation 35, $4LaS_2 = 2La_2S_3 + 2S(s)$ (35) as + 13.4 kcal. The difference in the heats of formation of LaS_2 and La_2S_3 can be derived from his measurements. Since neither NB-003 nor KU-001 gave a second reference the basis of their values were not clear. Kubaschewski's value was arbitrarily chosen.	-145.0
La_2S_3	-306.8 -282.0 ± 10	NB-003 (BI-002) KU-001 (NB-003)		-282.0

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
$MgCr_2O_4$	-421.19 ± 3.0 -302.4 -453.1 ± 2.4 -447.0	KU-001 (No Ref.) LA-001 (KA-003) CA-038 TR-002	The value reported by Landolt Boernstein, -302.4 kcal,was based on the work of Kapustinskii and co-workers (KA-003). However, on consulting the abstract for this publication it was found that the value -302.4 kcal was determined for magnesium oxalate, MgC_2O_4, instead of magnesium chromite, $MgCr_2O_4$. The heat of formation value published by Kubaschewski had no reference. The remaining value was obtained by Novakhatskii and co-workers (CA-038) from determination of the equilibrium constant of the reduction of magnesium chromite with hydrogen at 1200 to 1600° K. It was reported to have an accuracy of ± 2.4 kcal/mole. A reprint of the article has been ordered for translation. Since the value published by Novokhatskii was close to the TRACOR estimation, this value was adopted.	-453.1
$MgMoO_4$	-334.8 ± .2 -341.2 ± 1.2	CA-077 CA-076	The U.S. Bureau of Mines (CA-077) determined the heat of the reaction in Equation 36 using solution calorimetry. $MgO + MoO_3 \rightarrow MgMoO_4$ (36) The resulting heat of formation for $MgMoO_4$ was reported with an accuracy of ± 0.2 kcal. Rezukhina and co-workers (CA-076) determined the free energy change at 1100 to 1300° K for the reaction in Equation 37. $3Fe_{0.95}O + MgO + MoO \rightarrow MgMoO_4 + 3(0.95)Fe$ (37) The authors measured directly the heat capacity of $MgMoO_4$ and used published values for the other heat capacities for recalculation to 298.15° K. They reported an accuracy of ± 1.2 kcal. The value obtained by the U.S. Bureau of Mines using solution calorimetry (CA-077) is the accepted one.	-334.8
MoS_2	-55.97 -55.8 -60.4 ± 3.0	LA-001 (KU-005) NB-003 (KE-005) KU-001 (ST-001)	Landolt Boernstein cited Kubaschewski's 1951 edition (KU-005) which has since been revised (KU-001). The value given by the National Bureau of Standards was based on Kelley's Bulletin 406 (KE-005). His value was calculated using estimated heat capacity values, and was based on the pressure data of Parravano and Malquori (PA-002) which yielded "inconsistent ΔH values." Kubaschewski based his revised 1967 value on the work of Stubbles and Richardson (ST-001) who studied the equilibria between molybdenum sulfides and H_2S - H_2 gas mixtures using radioactive sulfur to prepare	-60.4

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
MoS_2 (continued)			the molybdenum sulfides and a counting technique to determine the H_2S equilibrium partial pressure. They also used Kelley's estimated heat capacity to calculate the heat of formation, and they estimated the error involved to be about 2 kcal. The value published by Kubaschewski is the accepted one.	
Mo_2S_3	-102.5 ± 7.2 -92.5 ± 4	LA-001 (KU-002) KU-001 (ST-001)	Values for the heat of formation of Mo_2S_3 cited by Landolt Boernstein (LA-001) and Kubaschewskii (KU-001) differ by 10 kcal. Landolt Boernstein gave an early edition of Kubaschewski's Metallurgical Thermochemistry (KU-002) for a reference. But since Kubaschewski rejected the earlier value in his 1967 edition, it would seem that his value of -92.5 kcal (KU-001) should be the accepted one. However, it was based on the equilibrium between molybdenum sulfides and H_2S measured radiochemically by Stubbles and Richardson (ST-001). From their measurements they calculated a heat of formation for MoS_2, but they report that the calculations cannot be made for Mo_2S_3 because of a lack of heat capacity data. Since Kubaschewski gave no heat capacity data for Mo_2S_3 in his tables, and since no such data has appeared in other literature, it is assumed that Kubaschewski estimated the heat capacity of the sulfide and used it to calculate the heat of formation from the vapor pressure data.	-92.5
Na_2S	-92.96 -89.2 -92.4 ± 2.0	LA-001 (KU-002) NB-003 (CO-002, RE-003, RE-005, KR-002) KU-001 (NB-003, RO-005)	All of the original literature has been consulted and it was found that all of the values are based ultimately on the previously mentioned work of Sabatier (SA-001) published in 1881. As mentioned in the discussion for barium sulfide, the heats of formation are based on the six-step Hess-Law summation with appropriate recalculations when one of the thermodynamic quantities included in the cycle was redetermined in later years with more accuracy. The early literature was often incomplete; the data lack error estimations. Temperatures at which the heats were measured are not given (evidently room temperature), and some of the determinations were carried out with materials only 96% pure with no corrections made for the impurities. We have decided to use the value published by Kubaschewski in his 1967 edition (KU-001), since: 1) it was close to the value published by Landolt Boernstein, and 2) it was the most recently published value and would, therefore, most probably have been recalculated using the most recently redetermined thermodynamic quantities.	-92.4

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
NiS	-17.48	LA-001 (NB-003)	The accepted value for the heat of formation of nickel monosulfide will be that published by Rosenquist (RO-004). In his discussion of the nickel-sulfur system, Rosenqvist commented on the work of other investigators. He stated that the results of Zakowskii and Jellinek (JE-001) were "of little value" since the authors failed to define the stoichiometry of the sulfide at equilibrium. He also stated that the equilibrium measurements of Schenck and von der Forst (SC-003) gave ratios of H_2S/H_2 pressure that were too high due to errors caused by thermal diffusion and measurements obtained from the cold zone. The value published by Landolt Boernstein is based on the data of the National Bureau of Standards (NB-003). The data used by the National Bureau of Standards were from a book published during the interval 1882 to 1886 (TH-001) and on an early paper by Schenck (SC-004). We did not read these references.	-20.2
	-22.2 ± 1.4	KU-001 (RO-004)		
	-17.5	NB-003 (SC-004, TH-001)		
	-20.2	RO-004		
Ni_3S_2	-43.35	LA-001 (NB-003)	The heat of formation of Ni_3S_2 will also be taken from the data of Rosenqvist (RO-004). Kubaschewski (KU-001) chose a value of -47.5 kcal based on Rosenqvist's measurements (RO-004) and this will be the accepted value for the TRACOR data base. The value given by Landolt Boernstein and the National Bureau of Standards was based on a Russian publication of 1939 (VA-001).	-47.5
		NB-003 (VA-001)		
	-47.5 ± 2.5	KU-001 (RO-004)		
PdO	-20.0	LA-001 (NB-003)	The accepted value for the heat of formation of palladium oxide will be that given in the recent review of Hepler and Goldberg (HE-002), $\Delta H_f^\circ = -27.6$ kcal. The value published in Landolt Boernstein, -20.0 kcal, and that of the National Bureau of Standards (NB-003) and Kubaschewski (KU-001) were all based on the early pressure determinations of Wohler (WO-003). The value given by Hepler and Goldberg (HE-002) was based on the recently published vapor pressure work of three independent authors (TA-001, SC-002,WA-002). At least one of these authors (TA-001) was aware of the work of Wohler. Hepler's value was an average of the values obtained from calculations using the data of the three authors cited above. Their values were -26.8 ± 2 kcal (TA-001), -28.35 ± 0.4 kcal (WA-002), and -27.5 kcal (SC-002).	-27.6
	-21.7 ± 1.5	KU-001 (WO-003)		
	-27.6	HE-002 (TA-001, SC-002, WA-002)		
		NB-003 (WO-003)		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
ReS_2	-33.2 ± 4	LA-001 (KU-002)	The best value for the heat of formation of rhenium sulfide was taken as -42.7 kcal (KU-001) based on the work of Cobble and McDonald (CA-074). These authors determined their value by heat of combustion measurements. The NBS value was based on the vapor pressure measurements of W. Biltz and co-workers (BI-001). It was pointed out by Cobble and McDonald that Biltz assumed the only gaseous species was sulfur, which casts doubt on his results since ReS_2 sublimes at around 1000° K. The value cited by Landolt Boernstein was based on an earlier publication of Kubaschewski which has since been revised.	-42.7
	-44.3	NB-003 (BI-001)		
	-42.7 ± 2.5	KU-001 (CA-074)		
RuS_2	-39.9 ± 3.6	LA-001 (KU-002)	Ruthenium, iron, and osmium are in the same column of the periodic table. For FeS_2 the heat of formation value of -42.4 kcal was accepted (KU-001) and for OsS_2 the value -24.5 (KU-001). One would expect the value of RuS_2 to be somewhere between these two extremes. The values listed by Kubaschewski and Landolt Boernstein, therefore, seem to be the more consistent values. Periodicity of the elements is the only reason that the value given by Kubaschewski was accepted. The value published in 1968 by Hepler (HE-002) casts doubt on the one of Kubaschewski since it was redetermined from the vapor pressure measurements of Juza and Meyer (JU-001)(1933) using Westrum's (WE-001) redetermined heat capacity equations.	-40.0
	-40.0 ± 3.5	KU-001 (KU-004)		
	-48.1	NB-003 (KE-005)		
	-53.0	HE-002 (WE-001)		
Sb_2O_4	-216.9 ± 1.1	CA-060	The values for heat of formation of Sb_2O_4 reported by Landolt Boernstein and the National Bureau of Standards were both based on the work of Simon and Thaler (SI-001) and Mixter (MI-001). The data were derived from equilibrium measurements of oxygen pressures for which individual determinations differed considerably. Also, the equations used to calculate the heat of reversible reactions at equilibrium do not take into account the heat capacity. It appears as if NBS but not Landolt Boernstein has recalculated the heat of formation from the temperature and pressure data with more accurate equations. Landolt Boernstein simply used the value of Simon and Thaler. The value was redetermined in 1962 by A. D. Mah of the U.S. Bureau of Mines (CA-060). The heat of combustion of antimony using bomb calorimetry was determined using pure antimony. The value obtained was -216.9 kcal with an accuracy of ± 1.1 kcal. This will be the accepted value for heat of formation of Sb_2O_4.	-216.9
	-214.0	NB-003 (SI-001, MI-001)		
	-195.2	LA-001 (SI-001)		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
Sb_2S_3	-38.22	LA-001 (KU-005)	Landolt Boernstein gave the 1951 edition of Kubaschewski's Metallurgical Thermochemistry (KU-005) as a reference. The sources cited by Kubaschewski in this edition, however, have nothing to do with Sb_2O_3. One is W. Kroll, Z. Anorg. Chem. 234, p. 42, (1937), which deals with the properties of titanium and zirconium compounds. As secondary references, Landolt Boernstein listed the same references (FR-001, BR-001, and BR-003) as given by NBS Circular 500 (NB-003). Britzke and Kapustinski (BR-003) compared their values to those obtained by another worker (Guenschant) who reportedly obtained a value of -38.2, exactly the value cited by Landolt Boernstein. These workers (BR-002) found a value of -42.5 kcal for the heat of formation of Sb_2S_3 from rhombic sulfur. They used, however, a value of -29.5 kcal for the heat of the reaction in Equation 38. $S_2(g) \rightarrow 2S(\text{Rhombic})$ (38) Using the accepted value of -31 kcal, their datum can be recalculated to give -41 kcal. This is apparently what was done by various workers since all of the data seem to be based on the same sources. In the 1967 edition of Kubaschewski's compilation, he gave the value -40.5 ± .5 which was essentially equal to the original value obtained by Britzke and Kapustinski, but recalculated using better data. This value will be the accepted one for the TRACOR compilation.	-40.5
	-40.5 ± 5.0	KU-001 (No Ref.)		
	-43.5	NB-003 (FR-001, BR-002, BR-003)		
	-41.8	NB-001 (No Ref.)		
Sc_2O_3	-447.3 ± 14.4	MA-003	The accepted value for the heat of formation of scandium sesquioxide (Sc_2O_3) is -456.16 kcal reported by Huber and Holley (HU-004). The value reported by A. D. Mah was obtained by combustion calorimetry as were Huber and Holley's data. Huber and Holley used a scandium oxide disc on which to carry out the combustion, while Mah used alundum. The work of Mah was repeated later with scandium metal supplied by Huber and Holley on an Sc_2O_3 disc,and the value she obtained fell within the range of values obtained by Huber and Holley (HU-004). The combustion on alundum was also repeated and the original results were obtained, indicating that the difference in the two values was caused by the alundum disc. The value published by Landolt Boernstein was taken from an early edition of Kubaschewski's Metallurgical Thermochemistry and has since been revised by Kubaschewski.	-456.16
	-456.16 ± 0.5	HU-004		
	-455.6 ± 1.5	KU-001 (HU-004)		
	-409.7	LA-001 (KU-002)		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
SiO_2 (quartz)	-205.28	LA-001 (NB-003)	In 1961 it was reported by J. Chipman that the accepted heat of formation of SiO_2 (quartz) was 5 kcal too high (CH-001). Several workers redetermined the value using substantially different methods. Wise (WI-002) using fluorine bomb calorimetry, and Good (GO-001), by redetermining the heat of formation of H_2SiF_6, obtained values which agreed well. Reznitskii (RE-002) obtained the heat of formation of the tridymite modification using EMF methods. He calculated the value for SiO_2 (quartz) to be some 4.5 kcal higher than that found by Wise and Good. He attributed the difference to the entropy of reaction calculated from the plot of EMF versus T and to the fact that some amorphous silica was probably formed and not taken into account. The value -217.7 quoted by both Kubaschewski and the National Bureau of Standards is considered to be the most reliable.	-217.7
	-213.17	RE-002		
	-217.7	NB-002		
	-217.0 ± 1.0	KU-001 (WI-002, GO-001)		
SrS	-112.9 ± 3.1	LA-001 (RO-006)	The literature cited by the major compilations is ultimately based on the early heat of solution measurements of Sabatier (1891) (SA-001). As mentioned previously, his data consisted of a six-step Hess' Law summation including various heats of solution and reaction. Several of these values have since been redetermined, therefore, we have chosen the value published by Kubaschewski since it was the result of the most recent evaluations.	-108.1
	-108.1	NB-003 (SA-001)		
	-108.1 ± 8.0	KU-001 (NB-003)		
Ta_2O_5	-499.5	LA-001 (HU-002)	For tantalum pentoxide the best value of the heat of formation was taken to be -488.5 kcal. Landolt Boernstein (LA-001) listed -2090.9 kJ or -499.5 kcal and gave Humphrey (HU-002) as a reference. Humphrey actually reported a value of -488.8 (HU-002), which agreed well with Huber and Holley's -488.5 (HU-003) and Kornilov and Leonidov's -489.3 (KO-001). Landolt Boernstein's value was possibly an error. If so, there is no conflict in the heat of formation values for Ta_2O_5.	-488.5
	-488.5 ± 1.0	KU-001 (HU-003)		
	-489.3	KO-001		
	-488.8	HU-002		
WO_2	-140.94 ± .21	JA-001 (MA-002)	Although several different values for the heat of formation of tungsten dioxide, WO_2, were reported in the open literature, the major compilations (LA-001, JA-001, KU-001) agreed that the value -140.9 kcal from calorimetric determinations (MA-002) was the most reliable, and it will be used in the TRACOR data base. The differing values are included in Table I even though all of the references have not been consulted. The contribution of Bousquet	-140.9
	-140.8	LA-001 (MA-002)		
	-140.9 ± 1.5	KU-001 (MA-002)		
	-136.6	CA-015		
	-133.0	BO-001		

TABLE I (continued)

CONFLICTING VALUES FOR THE STANDARD HEAT OF FORMATION OF INORGANIC COMPOUNDS

COMPOUND	VALUE (KCAL/MOLE)	REFERENCE	REMARKS	ACCEPTED VALUE (KCAL/MOLE)
WO_2 (continued)	-134.0	GR-001	and Perachon (BO-001) was important because it gave information on the complete tungsten-oxygen system including $WO_{2.72}$, $WO_{2.90}$, and $WO_{2.}$[illegible]. In some cases experimental findings have been invalidated because the author did not recognize or take into account the existance of all the possible ratios of number of metal to number of oxygen atoms. The EMF measurements of Gerasimov and co-workers (CA-015) yielded equilibrium data which were used along with a heat capacity equation accurate within 3% to calculate a heat of formation of -136.6 kcal. No limits of accuracy were given in the abstract.	
	-134.8	MO-001		
WS_2	-46.27	LA-001 (KE-005)	The references cited by Landolt Boernstein and Kubachewski (KE-005 and KU-003) for the heat of formation of tungsten disulfide both used the data of Parravano and Malquori (PA-001) to calculate a value for the heat of formation. Erdős (CA-070), Kelley (KE-005), and Kubaschewski (KU-003) all stated that the free energy data were only accurate to ± 10 kcal, and all three authors ascribed the error in the pressure data to the presence of thermal diffusion. Erdős redetermined the heat of formation value using EMF measurements at 15 to 45°C and from direct measurements in a flow apparatus at 350 to 500°C. His value of -53.97 kcal is considered the most reliable.	-53.97
	-46.27	NB-003 (RO-002)		
	-48.4 ± 4.0	KU-001 (KU-003)		
	-53.97	CA-070		
$ZnFe_2O_4$	-279.6 ± 1.0	CA-028	The heat of formation of zinc ferrite was reported in values differing by 7 kcal. Both investigators calculated heat of the reaction in Equation 39 from heats of solution. $ZnO + Fe_2O_3 \rightarrow ZnFe_2O_4 \qquad (39)$ The Russian authors (CA-042) determined heats of solution of ZnO, Fe_2O_3, and $ZnFe_2O_4$ in a mixture of sulfuric and phosphoric acids and found the heat of the above reaction to be -7 kcal. No error was given in the abstract. Fischer (CA-028) used solution calorimetry in sulfuric and phosphoric acids in the same manner. ZnO and Fe_2O_3 were dissolved and the heat of solution measured. Then pure $ZnFe_2O_4$ was dissolved and the heat measured. The difference in the two measured heats was taken to be the heat of the above reaction. The value determined was + 0.2 kcal. The estimated error was ± 1.0 kcal. The latter value was chosen because the authors gave an error estimation for their value.	-279.6
	-286.79	CA-042		

TABLE II

CONFLICTING VALUES FOR THE ABSOLUTE ENTROPY OF INORGANIC COMPOUNDS

COMPOUND	VALUE (e.u.)	REFERENCES	REMARKS	ACCEPTED VALUE (e.u.)
BaS	19.5	NB-003	The three published values differ only insignificantly. Kubaschewski (KU-001) based his value on Latimer's estimation (LA-002). The National Bureau of Standards (NB-003) gave no basis for its reported value. The value given by Landolt Boernstein was taken from a 1946 Russian publication which was not available to us. We do not know whether this value was estimated or measured. The Landolt Boernstein value was chosen because it is between the other two values.	20.9
	20.9	LA-001 (KI-001)		
	22.0 ± 3.0	KU-001 (LA-002)		
Ce_2O_3	30.8	CA-081	The value for the entropy of cerium sesquioxide has been determined by two independent authors to be 30.8 (CA-081) and 36.0 (CA-014) e.u. The value 36.0 e.u. determined by King and Weller (CA-014) was the accepted value for this work since their method was more direct and their errors were described. The entropy was determined directly from low temperature heat capacity measurements on cerium oxide of composition $Ce_2O_{3.33}$. The heat capacity data were corrected to Ce_2O_3 composition using the heat capacity values of Westrum and Beale (CA-066). The entropy was obtained by integration of the Cp versus log T plot and was reported to have an accuracy of ± 1 e.u. The value of Rezukhina and co-workers (CA-081) was determined from equilibrium measurements of dissociation pressures for cerium oxides of composition CeO_x, where $1.58 \leq x \leq 1.96$, using EMF techniques at temperatures from 900 to 1000°C. Their value was dependent on the heat capacity of CeO_2 and on the entropy of CeO_2 and O_2(g). They gave no estimation of accuracy.	36.0
	36.0	CA-014		
$CaTiO_3$	22.4 ± 0.2	KU-001 (KE-008, SH-001)	The value reported by Kubaschewski (KU-001), based on Kelley's Bureau of Mines Bulletin 477 (KE-008), is the one accepted for the TRACOR data base since it was determined by direct measurement. Kelley used the data of Shomate (SH-001) who measured the heat capacity of 99% pure $CaTiO_3$ from 52.5 to 298.2°K. The entropy from 0 to 52°K was obtained by extrapolation using the Debye-Einstein function. Graphical integration gave $S_{298} - S_{52} = 21.3$ e.u. and extrapolation gave $S_{52} = 1.08$ e.u. The resulting absolute entropy was 22.4 e.u. The value reported by Golubenko and Rezukhina (CA-053) was obtained by measuring the equilibrium of the following reaction in the range 1200 to 1300°K using EMF methods. $CaO + TiO_{0.5} + 0.75\ O_2 \rightarrow CaTiO_3$ (40)	22.4
	26.8	CA-053		

TABLE II (continued)
CONFLICTING VALUES FOR THE ABSOLUTE ENTROPY OF INORGANIC COMPOUNDS

COMPOUND	VALUE (e.u.)	REFERENCES	REMARKS	ACCEPTED VALUE (e.u.)
$CaTiO_3$ (continued)			In calculating the heat of formation and entropy of $CaTiO_3$, the properties of $TiO_{0.5}$ were estimated from those of other titanium compounds using the method of Karapet'yants (KA-002).	
$CaWO_4$	30.2 ± 0.2	KU-001 (KI-002)	The value reported by Kubaschewski (KU-001) was based on the U.S. Bureau of Mines work (KI-002) of King. The data were obtained by direct measurements of the heat capacity from 51 to 298° K. The data were extrapolated to absolute zero using the Debye-Einstein function. Simpson rule integration gave a value with 0.1% precision uncertainty and 5% uncertainty in the extrapolated portion. The value reported by Levitskii and co-workers (CA-025) was obtained from EMF measurements for the following equilibrium from 1140 to 1340° K. $CaO + WO_3 \rightarrow CaWO_4 \qquad (41)$ The abstract gave no error estimation. The value determined by the U. S. Bureau of Mines is the accepted one since it was obtained by direct measurements and was reported with an error estimation.	30.2
	27.0	CA-025		
Ir_2S_3	34.16	LA-001 (KU-002)	The values published by Kubaschewski and Landolt Boernstein were both estimated. The value reported by Hepler in his recent review of the platinum metals was based on vapor pressure measurements of Biltz (BI-003) which have been used by Westrum (WE-001) along with new heat capacity equations to redetermine the entropy value. Hepler's value was chosen since the others were estimated.	23.0
	34.2	KU-001 (LA-002)		
	23.0	HE-002 (BI-003, WE-001)		
NiS	16.1	LA-001 (KU-002)	The value of entropy for NiS published by Landolt Boernstein was based on Kubaschewski's 1959 edition (KU-002). In his 1967 edition (KU-001), however, Kubaschewski reported the value determined experimentally by the U.S. Bureau of Mines (CA-084). The heat capacity was measured directly from 50 to 298° K and reported with an accuracy of ± 0.08 e.u. This value is the one accepted for the TRACOR data base since the value reported by Landolt Boernstein has been revised by the original author.	12.66
	12.66 ± 0.08	KU-001 (CA-084)		
Ni_3S_2	36.57	LA-001 (KU-002)	The accepted value for the entropy of Ni_3S_2 is that determined by the U.S. Bureau of Mines by direct low temperature heat capacity measurement (CA-084). The value reported by Landolt Boernstein was based on Kubaschewski's 1959 edition (KU-002) which has since been revised.	32.0
	32.0 ± .2	KU-001 (CA-084)		

TABLE II (continued)

CONFLICTING VALUES FOR THE ABSOLUTE ENTROPY OF INORGANIC COMPOUNDS

COMPOUND	VALUE (e.u.)	REFERENCES	REMARKS	ACCEPTED VALUE (e.u.)
RuS_2	17.48	LA-001 (KU-002)	The values for the absolute entropy of RuS_2 published by Landolt Boernstein (LA-001) and Kubaschewski (KU-001) were estimated. The value accepted for the TRACOR data base is the one published in Hepler's review (HE-002). This value was based on vapor pressure measurements conducted by Juza and Meyer (JU-001) which were recalculated by Westrum (WE-001) using new heat capacity values. This value is also highly uncertain.	10.4
	17.5 ± 2.0	KU-001 (LA-002)		
	10.4	HE-002 (WE-001, JU-001)		
Sb_2S_3	39.6	LA-001 (KE-005)	The entropy of antimony sesquisulfide was given by Landolt Boernstein as 39.6 e.u. The value was taken from Kelley's Contributions to the Data on Theoretical Metallurgy No. XI, where the author stated that it was estimated from the heat and free energy equations given in Number VII, Bulletin 406, (1937). The U.S. Bureau of Mines, Report of Investigations No. 6040, (CA-073) reported the entropy to be 43.5 e.u. The National Bureau of Standards in its Technical Note 270-2 has also published the value of 43.5 e.u. and it will be the accepted value for the TRACOR data base. The entropy was found by Weller and King (CA-073) from measured rather than estimated values. The heat capacity of Sb_2S_3 of stoichiometric composition was measured from 50 to 295°K and from it, the entropy was calculated with an accuracy of ± 0.8 e.u.	43.5
	43.5 ± 0.8	NB-001 (CA-073)		
WS_2	20.0 ± 3.0	KU-001 (KU-003)	Landolt Boernstein gave NBS (NB-003) as a reference and NBS gave no reference. Kubaschewski (KU-001) gave his Thermodynamic Data of Alloys (KU-003) as a reference. There, he stated that the value of 20 e.u. was estimated by W. Latimer. Erdös (CA-070) had determined the thermodynamic properties of tungsten disulfide using two methods (see Table I). His value of 28.9 e.u. for the entropy was considered the best value value for the TRACOR data base, since the other values were either estimated or without a reference.	28.9
	22.9	LA-001 (NB-003)		
	23.0	NB-003		
	28.9	CA-070		

BIBLIOGRAPHY

AD-001 L. H. ADAMI, E. G. KING, U. S. BUR. MINES, REPT. OF INVEST. NO. 6617, (1965).

BA-001 R. F. BARROW, ET. AL., TRANS. FAR. SOC., VOL. 51, P. 1480, (1955).

BE-002 BERTHELOT, ESSAI DE MECANIQUE CHIMIQUE, PART 1, P. 319.

BI-001 W. BILTZ, Z. ELEKTROCHEM., VOL. 37, P. 498 (1931).

BI-002 W. BILTZ, Z. ANORG. CHEM., VOL. 71, P. 427 (1911).

BI-003 W. BILTZ, ET. AL., Z. ANORG. CHEM., VOL. 233, P. 257 (1937).

BO-001 J. BOUSQUET, G. PERACHON, COMPT. REND., VOL. 258, NO. 15, P. 3869 (1964).

BO-002 BOERICKE AND BANGERT, U. S. BUREAU OF MINES, REPT. OF INVEST. NO. 3813 (1945).

BR-001 L. BREWER, CHEMICAL REVIEWS, VOL. 52, P. 1 (1953).

BR-002 BRITZKE AND KAPUSTINSKII, Z. ANORG. CHEM., VOL. 194, P. 323, (1930).

BR-003 BRITZKE AND KAPUSTINSKII, J. PHYS. CHEM. (USSR), VOL. 5, P. 85, (1934).

BR-004 L. BREWER, L. BROMLEY, THE CHEMISTRY AND METALLURGY OF MISCELLANEOUS MATERIALS, (1950).

CA-014 CHEMICAL ABSTRACTS, 59:5860A W.W. WELLER, E.G. KING. U.S. BUR. MINES, REPT. INVEST. NO. 6245 (1963).

CA-015 CHEMICAL ABSTRACTS 55:8023B. YA. I. GERASIMOV, ET AL. DOKL. AKAD. NAUK SSSR VOL. 134, PP. 1350-2(1960).

BIBLIOGRAPHY (CONTINUED)

CA-019 CHEMICAL ABSTRACTS, 54:21971G. W.W. WELLER, E.G. KING, U. S. BUR. MINES REPT. INVEST. NO. 5590 (1960).

CA-021 CHEMICAL ABSTRACTS 64:16722G V.A. LEVITSKII, ET AL. ELEKTROKHIMIYA. VOL. 1, PP. 1371-4 (1965).

CA-025 CHEMICAL ABSTRACTS 65:950. V.A. LEVITSKII, ET AL. IZV. AKAD. NAUK SSSR NEORGAN. MATERIALY. VOL. 2, PP. 325-31 (1966). SEE TR-005.

CA-028 CHEMICAL ABSTRACTS 65: 9831C. M. FISCHER. Z. ANORG. ALLGEM. CHEM. VOL. 345, PP. 134-6 (1966).

CA-031 CHEMICAL ABSTRACTS 61:12705E. L. M. LENEV, I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, MET. I GORN. DELO, PP. 87-90 (1964) SEE TR-005.

CA-038 CHEMICAL ABSTRACTS 59:2473D. I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR OTD. TEKHN. NAUK, MET. I GORN. DELO 1963.

CA-042 CHEMICAL ABSTRACTS 55:11057C. L. A. REZNITSKII, K.G.KHOMYAKOV. DOKL. AKAD. NAUK SSSR. VOL. 31, PP. 325-6(1960). SEE TR-005.

CA-053 CHEMICAL ABSTRACTS 62:12509H. A.N. GOLUBENKO, T. N. REZUKHINA. ZH. FIZ KHIM. VOL. 38, PP. 2920-3 (1964).

CA-060 CHEMICAL ABSTRACTS 57:2927F. A. D. MAH U. S. BUR. MINES, REPT. INVEST. NO. 5972 (1962).

CA-066 CHEMICAL ABSTRACTS 56:1008H. E. F. WESTRUM, A. F. BEALE, J. PHYS. CHEM. VOL. 65, PP. 353-5 (1961).

CA-068 CHEMICAL ABSTRACTS 63:9122G. T. N. REZUKHINA, ET.AL., ELEKTROKHIMIYA VOL.1, PP.467-71 (1965). SEE TR-005.

CA-070 CHEMICAL ABSTRACTS, 54:10465F. E.ERDOS, ET AL. COLL. CZECH. CHEM. COMMUN., VOL.24, PP. 3836-43(1959).

BIBLIOGRAPHY (CONTINUED)

CA-071 CHEMICAL ABSTRACTS,54:14904E. K.M.KOLBINA, ET AL. VESTNIK LENINGRAD UNIV., VOL.15, SER. KHIM. I FIZ., PP. 122-9(1960).

CA-073 CHEMICAL ABSTRACTS,57:13234C. W.W.WELLER, E.G.KING, U.S. BUR. MINES, REPT. INVEST. NO 5040 (1962).

CA-074 CHEMICAL ABSTRACTS,57:2927G. J.W.COBBLE,J.E.MCDONALD, J. PHYS. CHEM., VOL.66, P.791(1962).

CA-076 CHEMICAL ABSTRACTS,58:8459B. T.N. REZUKHINA, ET AL, ZH. FIZ. KHIM., VOL. 35, PP.2639-42 (1961).

CA-077 CHEMICAL ABSTRACTS,58:5102C. R. BARANY, U. S. BUR. MINES, REPT. INVEST. NO 6143 (1962).

CA-081 CHEMICAL ABSTRACTS,59:1256B. H. SCHAEFER, ET AL., Z. ANORG. ALLG. CHEM., VOL. 321, PP. 41-55 (1963).

CA-084 CHEMICAL ABSTRACTS,61:12709B. K.K. KELLEY, W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 6511 (1964).

CH-001 J. CHIPMAN, J. AM. CHEM. SOC., VOL. 83, P. 1762 (1961).

CH-002 J. CHIPMAN, H. M. CHAN, TRANS. AMER. SOC. METALS, VOL. 38, P. 70 (1947).

CO-002 COURTOIS AND GASTEN, COMPT. REND., VOL. 207, P. 1220 (1938).

ER-003 E. ERDOS, 'EQUILIBRIA IN THE SYSTEMS SO2-CO2-MO,' COLL. CZECH. CHEM. COMMUN., VOL. 27, P. 2152-67 (1962).

FR-001 FRICKE AND DONGES, Z. ANORG. CHEM., VOL. 250, P. 202 (1942).

GO-001 W. D. GOOD, J. PHYS. CHEM., VOL. 66, P. 380 (1962).

GR-001 R. C. GRIFFIS, J. ELECTROCHEM. SOC., VOL. 106, P. 418 (1959).

BIBLIOGRAPHY (CONTINUED)

HE-002 L.G.HEPLER, R.N.GOLDBERG, CHEM. REVIEWS, VOL. 68, PP. 229-52(1968).

HE-003 L. G. HEPLER, C. N. MULDROW, J. PHYS. CHEM., VOL.62, P. 982 (1958).

HI-001 C. HIRAYAMA, J. CHEM. ENG. DATA, VOL. 9, P. 65 (1964).

HU-001 E.J. HUBER, C.E. HOLLEY, J. AM. CHEM. SOC., VOL. 75, P. 3594, (1953).

HU-002 G.L. HUMPHREY, J. AM. CHEM. SOC., VOL. 76, P. 978 (1954).

HU-003 E. J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 793 (1963).

HU-004 E.J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 1731 (1963).

HU-006 E.J. HUBER, C. HOLLEY, J. CHEM. ENG. DATA, VOL. 13, P. 252 (1968).

HU-007 G. L. HUMPHREY, J. AM. CHEM. SOC., VOL. 75, P. 2806 (1953).

HU-008 E.J. HUBER, C. HOLLEY, J. AM. CHEM. SOC., VOL. 77, P. 1444 (1955).

JA-001 JANAF THERMOCHEMICAL TABLES,THE DOW CHEMICAL CO.,MIDLAND,MICHIGAN, AUG.,1965.

JE-001 K. JELLINEK, J. ZAKOWSKII, Z. ANORG. CHEM., VOL. 142, PP.1-53, (1925).

JO-001 H.L. JOHNSTON, ET. AL., J. AM. CHEM. SOC., VOL. 73, P. 1112, (1951).

JU-001 JUZA AND MEYER, Z. ANORG. CHEM., VOL. 213, P. 273 (1933).

KA-001 KAPUSTINSKII AND GOLUTWIN, IZVEST. AKAD. NAUK SSSR, OTDEL KHIM. NAUK, P. 192 (1951).

KA-002 M. KARAPET'YANTS, ZH. FIZ. KHIM., VOL. 30, P. 593 (1956).

BIBLIOGRAPHY (CONTINUED)

KA-003	A. F. KAPUSTINSKII, O. SAMOILOV, IZV. AKAD. NAUK SSSR, OTD. KHIM. NAUK, P. 337-43 (1950). CHEM. ABSTRACTS,44:9790F.
KE-005	K. K. KELLEY, CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY, U.S. BUREAU OF MINES BULLETIN 406, (1937).
KE-008	K. K. KELLEY, THE ENTROPIES OF INORGANIC SUBSTANCES: REVISION OF DATA, U. S. BUREAU OF MINES BULL. 477(1950).
KI-001	W. A. KIREJEW, J. CHIM. GEN. (USSR), VOL. 16, P. 1569, (1946).
KI-002	E. G. KING, W. W. WELLER, U. S. BUR. MINES, REPT. OF INVEST. NO. 5791 (1961).
KL-001	KLEMM AND SCHNICK, Z. ANORG. CHEM., VOL. 226, P. 353 (1936).
KO-001	KORSHUNOV, J. PHYS. CHEM.(U.S.S.R.), VOL. 13, P. 703 (1939).
KR-002	KRAUS AND RIDDERHOFF, J. AM. CHEM. SOC., VOL. 56, P. 79 (1934).
KU-001	O. KUBASCHEWSKI, ET AL . METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS 4TH EDITION (1967).
KU-002	O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS, (1959).
KU-003	O. KUBASCHEWSKI , THERMO. DATA OF THE ALLOYS, PERGAMON PRESS, (1956).
KU-004	KUBASCHEWSKI AND WEIBKE, THERMOCHEMIE DER LEGIERINGEN, SPRINGER, BERLIN, 1943.
KU-005	O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEKISTRY, PERGAMON PRESS, (1951).
LA-001	KALORISCHE ZUSTANDGROESSEN IN 'LANDOLT BOERNSTEIN',SPRINGER-VERLAG, BERLIN,VOL.2,PART4(1961).

BIBLIOGRAPHY (CONTINUED)

LA-002 W. LATIMER, J. AM. CHEM. SOC., VOL. 73, P. 1480 (1951).

LE-003 LEVITSKII, ET AL., RUSS. J. PHYS. CHEM., VOL. 35, NO. 6, P. 671 (1961)

MA-002 A. D. MAH, J. AM. CHEM. SOC., VOL. 81, P. 1582 (1959).

MA-003 A.D. MAH, U. S. BUR. MINES, REPORT OF INVESTIGATIONS NO. 5965, (1962).

MA-005 MARCHAL, J. CHIM. PHYS., VOL. 23, P. 38, (1926).

ME-001 G. MEYER, E.H.P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 670, (1962).

ME-003 G. MEYER, E. H. P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 495 (1962).

MI-001 MIXTER, AM. J. SCI. , VOL. 28, P. 103 (1909).

MO-001 M. P. MOROZOVA, L. GETSKINA, VESTNIK LENINGRAD. UNIV., VOL. 14, NO. 22, SER. FIZ. I KHIM. NO. 4, VOL. 128, (1959).

MO-002 A. N. MOROZOVA, N. A. NOVOKHATSKII, IZV. A N SSSR, OTD. TEKHN. N., METALLURGIYA I TOPLIVO, NO. 6, P. 3 (1962).

NB-001 SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART I,NATIONAL BUREAU OF STANDARDS,1965.

NB-002 SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART II,NATIONAL BUREAU OF STANDARDS,1966.

NB-003 F,ROSSINI,ET AL. SELECTED VALUES OF CHEM. THERM. PROPERTIES, NATL. BUREAU OF STANDARDS, CIRCULAR 500, (1952).

NB-005 SELECTED VALUES OF CHEM. THERM. PROPS., NATNL. BUR. STDS., TABLES FOR FIRST 34 ELEMENTS IN STD. ORDER OF ARRANGEMENT. TN 270-3 (1968).

BIBLIOGRAPHY (CONTINUED)

PA-001 N.PARRAVANO, G.MALQUCRI, ATTI. R. ACAD. LINCEI, SER. 6, VOL. 7, P. 189 (1928).

PA-002 PARRAVANO AND MALQUORI, ATTI. REND. ACCAD. LINCEI, SER. 6, VOL. 7, P. 109 (1928).

RE-002 L.A. REZNITSKII, ZH. FIZ. KHIM., VOL. 38, P. 760 (1964).(CHEMICAL ABSTRACTS,61:8004F.)

RE-003 RENEGADE AND CONSTEANU, BULL. SOC. CHIM. FRANCE, VOL. 15, P. 717 (1914).

RE-005 RENEGADE AND CONSTEANU, COMPT. REND., VOL. 158, P. 946 (1914).

RO-001 W. ROTH, Z. ELEKTROCHEM., VOL. 46, P. 42 (1940).

RO-002 W.ROTH, ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA,XI, SECT. 12, 'THERMOCHEMISTRY (1931-1934),' HERMANN AND CO., PARIS, (1937).

RO-003 W. ROTH, G. BECKER, Z. PHYSIK. CHEM., VOL. A159, P. 1 (1932).

RO-004 T. ROSENQVIST, J. IRON AND STEEL INSTITUTE, VOL. 176, P. 36, (1954).

RO-005 W.A. ROTH, F I A T REPORTS OF GERMAN SCIENCE, INORG. CHEM., VOL. 4, P. 214 (1948).

RO-006 ROSSINI AND BICHOWSKY, THERMOCHEMISTRY OF CHEMICAL SUBSTANCES, NEW YORK (1936).

SA-001 P. SABATIER, ANN. CHIM. PHYS., VOL. 22, P.5 (1881).

SC-001 H. SCHAEFER, H. HEITLAND, Z. ANORG. CHEM., VOL. 304, P. 249, (1960).

SC-002 N. G. SCHMALL, E. MINZL, Z. PHYSIK. CHEM. (FRANKFURT), VOL. 47, P. 142 (1965).

BIBLIOGRAPHY (CONTINUED)

SC-003 R. SCHENCK, P.VON DER FORST, Z. ANORG. CHEM., VOL. 241, PP. 145-57, (1939).

SC-004 SCHENCK AND RAUB, Z. ANORG. CHEM., VOL. 178, P. 225 (1929).

SH-001 C. SHOMATE, J. AM. CHEM. SOC., VOL. 68, PP. 964-6 (1946).

SH-002 SHOMATE, NAYLOR, AND BOERICKE, U. S. BUR. MINES, REPT. INVEST. NO. 3864 (1946), J. AM. CHEM. SOC., VOL. 68, P. 1003 (1946).

SI-001 SIMON AND THALER, Z. ANORG. CHEM., VOL. 162, P. 253 (1927).

ST-001 J.R. STUBBLES, F.D. RICHARDSON, TRANS. FARADAY SOC., VOL. 56, P. 1460 (1960).

SU-001 K. SUDO, SCIENCE REPT. RESEARCH INST. TOHOKU UNIV., SER.A, VOL. 2, P. 507 (1950).

TA-001 M. TAGAMI, W. BELL, J. PHYS. CHEM., VOL. 70, P. 3735 (1960).

TH-001 THOMSEN, THERMOCHEMISCHE UNTERSUCHUNGEN, BARTH, LEIPZIG (1882-1886).

TR-002 TRACOR VALUE ESTIMATED USING MODIFIED ERDOS METHOD, SEE TECHNICAL MEMORANDA 004-009-CH1 AND 004-009-CH1A.

VA-001 V. A. VANYUKOV, N. A. KISELEVA, YUBELEINYI SBORNIK TRUDOV KAFEDRY I LAB. TYAZHELYKH METALLOV MOSKOV. INST. TSVETNYKH METALLOV I ZOLOTA NO. 7, P. 304, (1939).

WA-001 VON WARTENBERG, Z. ANORG. CHEM., VOL. 71, P. 427 (1911).

WA-002 J. S. WARNER, J. ELECTROCHEM. SOC., VOL. 114, P. 68 (1967).

WE-001 WESTRUM, ET AL., J. CHEM. PHYS., VOL. 35, P. 1670 (1961).

BIBLIOGRAPHY (CONTINUED)

WI-002 WISE, ET. AL., J. PHYS. CHEM., VOL. 66, P. 381 (1962).

WO-001 WOHLER AND WITZMAN, Z. ELEKTROCHEM., VOL. 14, P. 97 (1908).

WO-002 WOHLER AND JOCKUM, Z. PHYSIK. CHEM., VOL. A167, P. 169 (1933).

WO-003 WOHLER, ZH. FIZ. KHIM., VOL. 167, P. 176 (1933).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

8 July 1968 P. S. Lowell/G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-CH7

STABILITY OF OXIDES IN A FLUE GAS ATMOSPHERE

The stability of dry metal oxides under typical furnace flue gas conditions was investigated.

For those metal oxides under consideration having only one oxidation state, the dissociation reaction to the metal and oxygen was written. Also for those metal oxides under consideration exhibiting multiple oxidation states the dissociation reaction to the metal and oxygen for each oxidation state of the metal oxide was written. The Gibbs standard free energy change was calculated for each reaction by using the following relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where

$$\Delta H^\circ = \Delta H^\circ_{298} + \sum_{pt} \Delta H_{pt} + \int_{298}^{T} Cp dT$$

$$\Delta S^\circ = \Delta S^\circ_{298} + \sum_{pt} \frac{\Delta H_{pt}}{T_{pt}} + \int_{298}^{T} \frac{Cp}{T} dT$$

$$Cp = A + BT + CT^2 - D/T^2$$

The standard state of oxygen was chosen to be 0.028 ATM corresponding to the partial pressure of oxygen in a typical furnace flue gas mixture. Thus the standard entropy value was corrected to this standard state from the usual 1 ATM by the following equation:

$$\Delta S^\circ_p = \Delta S^\circ + nR \ln \frac{P}{P_p} = \Delta S^\circ + nR \ln\left(\frac{1}{0.028}\right)$$

With the standard Gibbs free energy calculated using the corrected standard entropy values, the equilibrium constant was then calculated using the following relationship:

$$\Delta G^\circ = -RT \ln K = -2.303RT \log K$$

A plot of log K vs temperature was prepared for each dissociation reaction under consideration. The above mentioned calculations and plots were made utilizing the Univac 1108 Digital Computer. The temperature range considered was 25° C to 750° C. This temperature range was chosen in order to include the most probable operating conditions of SO_2 removal equipment in furnace flue gases.

To determine which metal oxide form is the most stable for those metal oxides under consideration having multiple oxidation states the principle of treating thermochemical equations like algebraic equations was applied to combining Gibbs free-energy equations.

To determine which lead oxide, either PbO or PbO_2, is the more stable form the following reaction can be written:

$$PbO_2 \rightleftharpoons \tfrac{1}{2}PbO + \tfrac{1}{2}O_2 \quad \Delta G^\circ = \Delta G_3^\circ$$

The sign of ΔG° indicates which direction is favored.

The same results may be obtained by writing the decomposition reactions of PbO_2 and PbO to the metal and oxygen.

(1) $PbO_2 \rightarrow Pb + O_2 \quad \Delta G^\circ = \Delta G_1^\circ$

(2) $PbO \rightarrow Pb + \tfrac{1}{2}O_2 \quad \Delta G^\circ = \Delta G_2^\circ$

and subtracting equation (2) from equation (1) to obtain the reaction under consideration:

(3) $PbO_2 \rightarrow PbO + \tfrac{1}{2}O_2 \quad \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$

The Gibbs free-energy change for equation (3) can be obtained by comparing the Log K vs temperature plots of the decompositon reactions of PbO_2 and PbO. Thus from Figure 1 it is seen that PbO_2 is the more stable up to 268° C and PbO is the more stable from 268° C to 750° C.

By writing the decomposition reactions in the above form, several computations can be saved. In comparing four oxide forms the number of combinations of N oxide forms taken two at a time would be given by the following equation:

$$\frac{N!}{R!(N-R)!} = \frac{4!}{2!(4-2)!} = 6$$

Therefore, all six of the reactions needed to compare the four oxide forms can be obtained by graphical comparison of the four oxide decomposition reactions to their metal and oxygen.

A table was prepared listing the various multiple metal oxides that were under consideration. Also indicated in the table is the most stable oxide form and at what temperature range it is the most stable.

G. D. Schroeder
P. S. Lowell

DRY METAL OXIDES WITH MULTIPLE OXIDATION STATES

COMPOUND	STABLE OXIDE FORM From t° C	STABLE OXIDE FORM To t° C
Ce_2O_3	25	750
CeO_2		
CoO	739	750
Co_3O_4	25	739
Cu_2O		
CuO	25	750
FeO		
Fe_3O_4		
Fe_2O_3	25	750
MnO		
Mn_3O_4		
Mn_2O_3	390	750
MnO_2	25	390
PbO	268	750
PbO_2	25	268
Rh_2O	576	750
RhO		
Rh_2O_3	25	576

COMPOUND	STABLE OXIDE FORM From t° C	To t° C
SnO		
SnO_2	25	750
TiO		
Ti_2O_3		
TiO_2	25	750
Ti_3O_5		
UO_2		
U_3O_8	544	750
UO_3	25	544
VO		
V_2O_3		
V_2O_4		
V_2O_5	25	750
WO_2		
WO_3	25	750

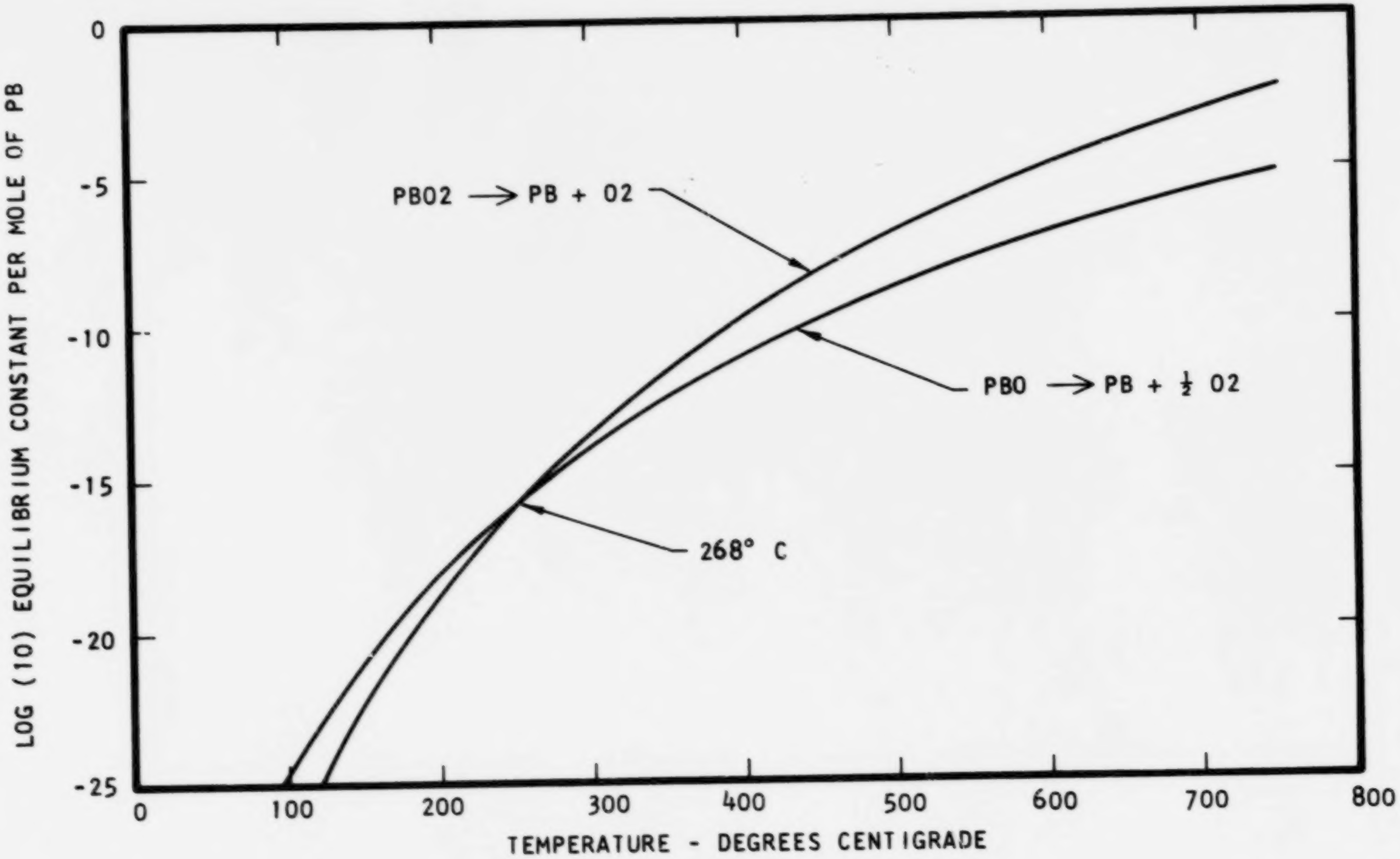


FIG. 1 - DECOMPOSITION OF LEAD OXIDES
STANDARD STATE OF O2 IS 0.028 ATM

TRACOR DWG. A6-3-659
7/11/68 SD / SCHROEDER

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

TECHNICAL MEMORANDUM 004-009-CH8
22 August 1968

K. Schwitzgebel

STABILITY AND DECOMPOSITION OF SULFATES

TABLE OF CONTENTS

I. INTRODUCTION 1

II. THERMAL DECOMPOSITION OF SULFATES. 2

III. EXPERIMENTAL TECHNIQUES. 4

IV. OXIDES USED AS CATALYSTS IN SO_2-SO_3 OXIDATION. 15

V. REDUCTIVE DECOMPOSITION OF SULFATES. 19

VI. SUMMARY. 30

LITERATURE

TABLE I

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

22 August 1968 K. Schwitzgebel

TECHNICAL MEMORANDUM 004-009-CH8

STABILITY AND DECOMPOSITION OF SULFATES

I. INTRODUCTION

The disproportionation of sulfites to sulfides and sulfates on heat was discussed in Technical Memorandum 004-009-CH3. The thermal stability of the sulfates and sulfides and their behaviour under reductive or oxidative conditions is important in the regeneration step of the process under investigation. This memorandum gives the results of a literature search concerning the stability of sulfates.

The commonly used experimental methods of investigation are described briefly. The possibility of oxidizing SO_2 during formation of sulfites with catalytic effective oxides is discussed. This process would be of interest if the resulting sulfate could be decomposed thermally. A survey of the processes of reductive decomposition of sulfates is given.

II. THERMAL DECOMPOSITION OF SULFATES

The U.S. Department of Commerce recently published a literature survey [1] concerning the high temperature properties and decomposition of inorganic salts. The survey covers the literature up to 1962 and in some cases, 1964. Many articles which have appeared recently concerning the thermal behaviour of sulfates are not included in the Department of Commerce survey. Table I gives a survey of the literature on the thermal behaviour of the sulfates including those newer publications. It is difficult to compare the behaviour of the different sulfates since not all experiments were run under identical conditions. There were two different experimental procedures. One type was carried out under static conditions. After evacuation at low temperature the samples were heated and allowed to reach their equilibrium pressure. The second type was conducted under dynamic conditions. These experiments were run in neutral atmospheres such as nitrogen or argon, or in oxidizing atmospheres such as air. The literature results as presented in Table I must therefore be applied with same care to our problem. With this restriction in mind, the sulfates can be divided into four groups: 1) sulfates which show a simple decomposition accompanied by the formation of the corresponding oxides; 2) sulfates which decompose to the oxides with the intermediate formation of oxysulfates; 3) sulfates which decompose with oxidation; and 4) sulfates which decompose with reduction (the final products are the metals). Naturally this grouping is crude, since the decomposition path is influenced by the experimental condition and especially the atmosphere.

The first group (see Table I) includes the sulfates of the following elements: Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Hf, V^{3+}, (see table), Fe^{3+}, Al, Ga, Sn^{4+}, and Th.

The second group includes the sulfates of the following metals: Y (forms $Y_2O_2(SO_4)$), La ($La_2O_2(SO_4)$), Ce^{3+}, Ti ($TiOSO_4$), V^{4+} ($VO(SO_4)$), V^{5+} ($V_2O_5 \cdot xSO_3$), Cr ($Cr_2O(SO_4)_2$), Mn ($Mn_2O(SO_4)_2$), [Fe^{3+} ($Fe_2O_2(SO_4)$) see table], Co (Co_2OSO_4), Cu^{2+} ($CuO \cdot CuSO_4$), Zn ($ZnO \cdot 2ZnSO_4$), Cd ($CdSO_4 \cdot 2CdO$), Pb ($PbSO_4 \cdot xPbO$, x=1, 2, or 4), Bi ($Bi_2O_3 \cdot 2Bi_2(SO_4)_3$; $2Bi_2O_3 \cdot Bi_2(SO_4)_3$; $3Bi_2O_3 \cdot Bi_2(SO_4)_3$. The results of Bela Lorant [14] should be used with care. Bela Lorant worked with thermogravimetric analysis. The formulas for the oxysulfates he gives are based on stoichiometric calculations only.

The elements belonging to Group 3 are: Mn^{2+} and Mn^{3+}, Fe^{2+}, Co, Ni, Cu^{1+}, Sn^{2+}, and U.

The fourth group includes the noble metals, Pd, and Ag.

No papers were found in the literature describing the decomposition mechanism for the sulfates of the following metals: Nb, Ta, Mo, W, Ru, Re, Rh, Ir, B, Si, Ge, and As. The sulfates of Ru, Re, Rh, and Ir will probably belong to Group 4. Of the remaining sulfates, the behaviour of Nb-, Ta-, Mo-, and W- sulfate would be of special interest. Nb, Ta, and W, like vanadium might be effective as catalysts in the oxidation of SO_2.

III. EXPERIMENTAL TECHNIQUES

The results shown in Table I were mostly obtained by DTA, TGA, and GA. These methods are well described in the "Proceedings of the First Toronto Symposium on Thermal Analysis" [29]. These methods provide means of measuring transition points, transition heats, decomposition temperatures, and reaction kinetics. The heats of activation determined in these dynamic experiments however are often too high as pointed out by T. R. Ingraham [30]. Table II [31] gives an idea of the order of magnitude.

TABLE II

Comparison of Heats of Reaction with Enthalpies of Activation Determined by Isothermal and Linearly Programmed Temperature Experiments

Reaction	$\Delta H^{\ddagger}_{iso}$	$\Delta H^{\ddagger}_{lin}$	$\Delta H^{\ddagger}_{lin} - \Delta H^{\ddagger}_{iso}$
$BaCl_2.2H_2O \rightleftarrows BaCl_2.H_2O + H_2O$	16	19	3
$BaCl_2.H_2O \rightleftarrows BaCl_2 + H_2O$	18	26	8
$CaCO_3 \rightleftarrows CaO + CO_2$	41	48	7
$2CuSO_4 \rightleftarrows CuO.CuSO_4 + SO_3$	54	71	17
$CuO.CuSO_4 \rightleftarrows 2CuO + SO_3$	67	68	-

T. R. Ingraham, "Making Decomposition Rate Measurements on Simple Inorganic Chemical Powders by T.G.A.". Proceedings of the First Toronto Symposium on Thermal Analysis, pp. 81-99, H. G. McAdie, Ed., Toronto Section, Chem. Inst. of Canada, Feb. 8, 1965.

Deviations are caused by the fact that the decomposition products are often amorphous, whereas the thermodynamic functions are based on the crystalline state. For a complete thermodynamic treatment of the decomposition reactions, the heat of formation, absolute entropy and the heat capacity equations of all compounds are necessary. Unfortunately these values are unknown for many oxysulfates (see Group 2, Part 2). A technique commonly used to determine the heats of reaction involved is static vapor pressure measurement. A difficulty involved in this technique is the fact that SO_2 and SO_3 are corrosive. Therefore the commonly employed U-bend mercury manometer cannot be used. S. N. Flengas and T. R. Ingraham [32] developed an apparatus using a glass-bellows mercury manometer which was described earlier by R. Spence [33]. Figure 1 shows the apparatus used by A. H. Warner and T. R. Ingraham in their experiments to determine decomposition pressures of ferric sulfate and aluminum sulfate [34]. The equilibrium pressure for a given temperature was reached from both sides (heating and cooling experiments). A plot of $-R\ln p_{SO_3}$ versus $1/T$ gives a straight line. Figure 2 shows the results of T. R. Ingraham and H. H. Kellogg [24] for the decomposition of α and β $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$.

It is always assumed that the reaction

$$SO_3 \rightleftharpoons SO_2 + \tfrac{1}{2}O_2$$

has reached equilibrium. From equilibrium pressures as a function of temperature the heat of formation and absolute entropy can be calculated using Kelley's Σ-function method [35].

With this experimental procedure the following systems were investigated: Pb-S-O[27], Cu-S-O[36], Mn-S-O[37], Fe-S-O[38], Co-S-O[39], Zn-S-O[24], and Ni-S-O[40]. These experimental results seem to be the most reliable ones found in the literature, Figures 3-9 show the resulting phase diagrams. The method of construction is described by Kellogg and Basu [27].

A critical review of sulfation equilibriums was given by H. H. Kellogg in 1964 [41].

WARNER AND INGRAHAM: FERRIC SULPHATE AND ALUMINUM SULPHATE 2197

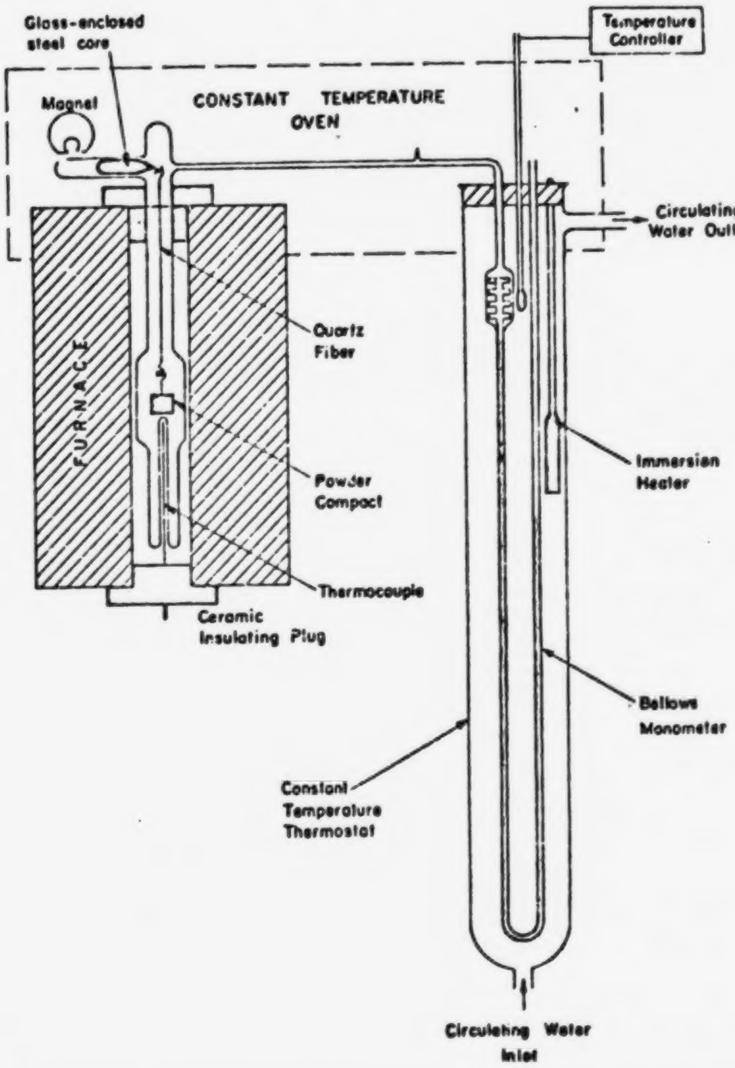
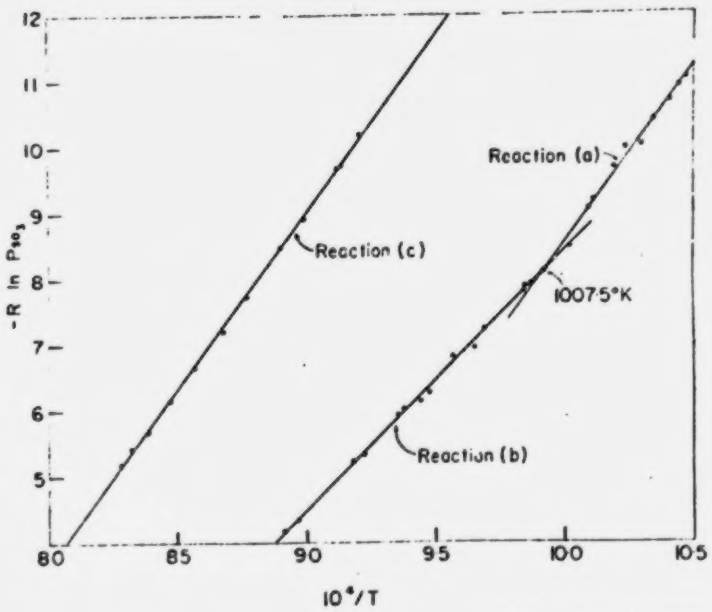

Glass-enclosed steel core
Temperature Controller
Magnet
CONSTANT TEMPERATURE OVEN
Circulating Water Outlet
FURNACE
Quartz Fiber
Powder Compact
Immersion Heater
Thermocouple
Ceramic Insulating Plug
Bellows Monometer
Constant Temperature Thermostat
Circulating Water Inlet

FIG. 1. Apparatus for measuring decomposition pressures of anhydrous sulphates. [34]

A. N. Warner, T. R. Ingraham, "Decomposition Pressures of Ferric Sulphate and Aluminum Sulphate", Can. J. Chem., vol. 38, pp. 2196-202 (1960).

Figure 2 [24]



Relation between temperature and the partial pressure of SO_3 calculated from total pressure measurements. Reactions (a), (b), and (c) refer to reaction equations in the text.

T. R. Ingraham, H. H. Kellogg, "Thermodynamic Properties of Zinc Sulfate, Zinc Basic Sulfate, and the System Zn-S-O", Trans. AIME, vol. 227, pp. 1419-26 (1963).

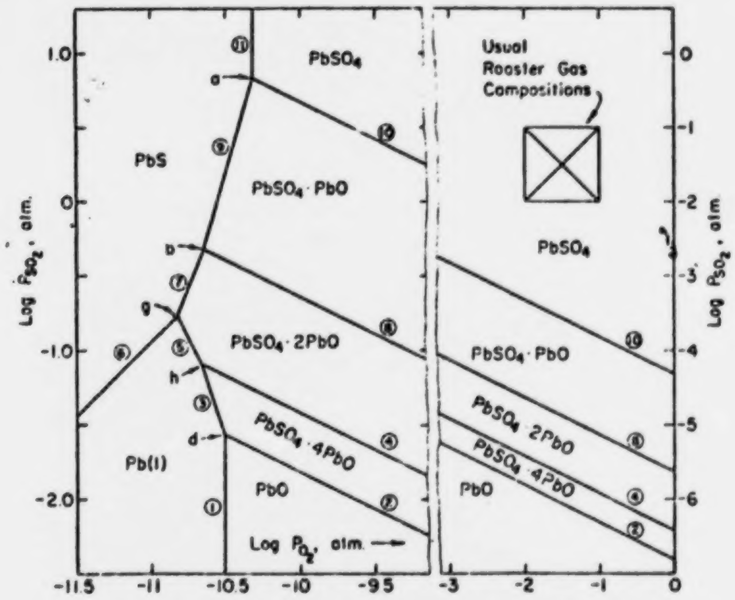
The reactions corresponding to the pressures shown in Figure 2 are:

a) $3ZnSO_4(\alpha) \rightleftharpoons ZnO\cdot 2ZnSO_4(c) + SO_3$

b) $3ZnSO_4(\beta) \rightleftharpoons ZnO\cdot 2ZnSO_4(c) + SO_3$

c) $\frac{1}{2}(ZnO\cdot 2ZnSO_4)(c) \rightleftharpoons \frac{3}{2} ZnO + SO_3$

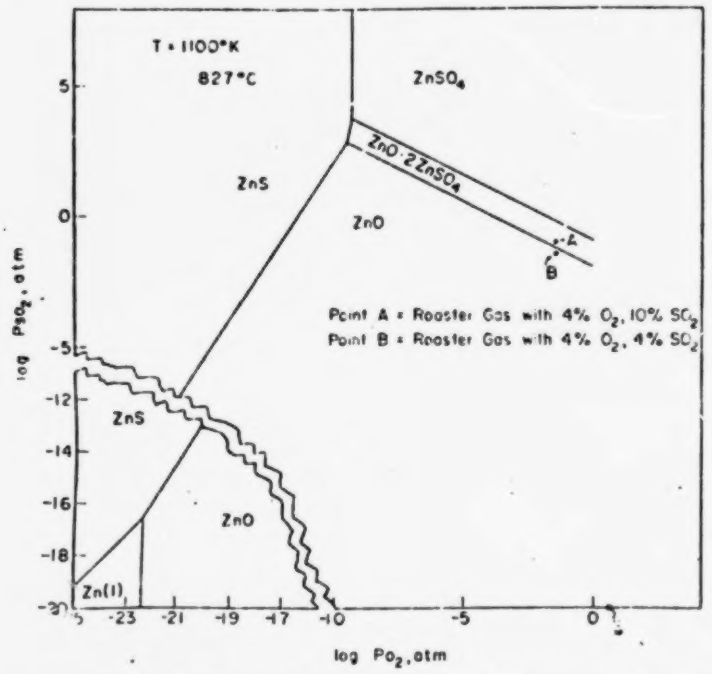
Figure 3 [27]



—Thermodynamic Phase Diagram for Pb-S-O showing bivariant equilibria at 1100°K. Letters refer to univariant equilibria; numbers refer to bivariant equilibria. Areas show regions of stability of a single condensed phase.

H. H. Kellogg, S. K. Basu, "Thermodynamic Properties of the System Pb-S-O to 1100°K", Trans. AIME, vol. 218, pp. 70-81 (1960).

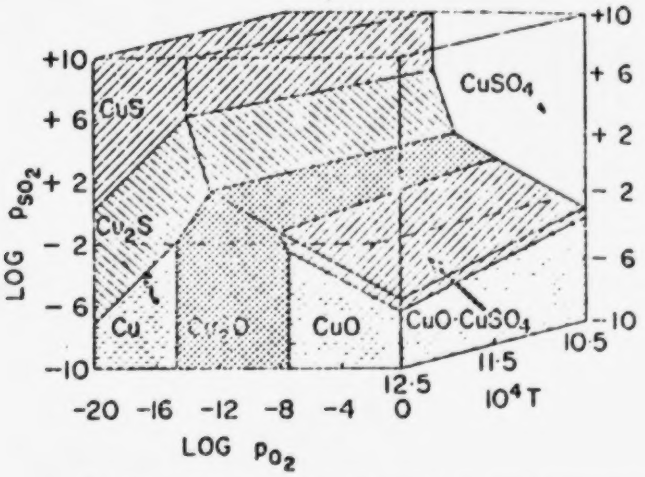
Figure 4 [24]



Stable bivariant equilibria in the system Zn-S-O at 1100°K. Areas are regions of stability of one condensed phase as marked.

T. R. Ingraham, H. H. Kellogg, "Thermodynamic Properties of Zinc Sulfate, Zinc Basic Sulfate, and the System Zn-S-O", Trans. AIME, vol. 227, pp. 1419-26 (1963).

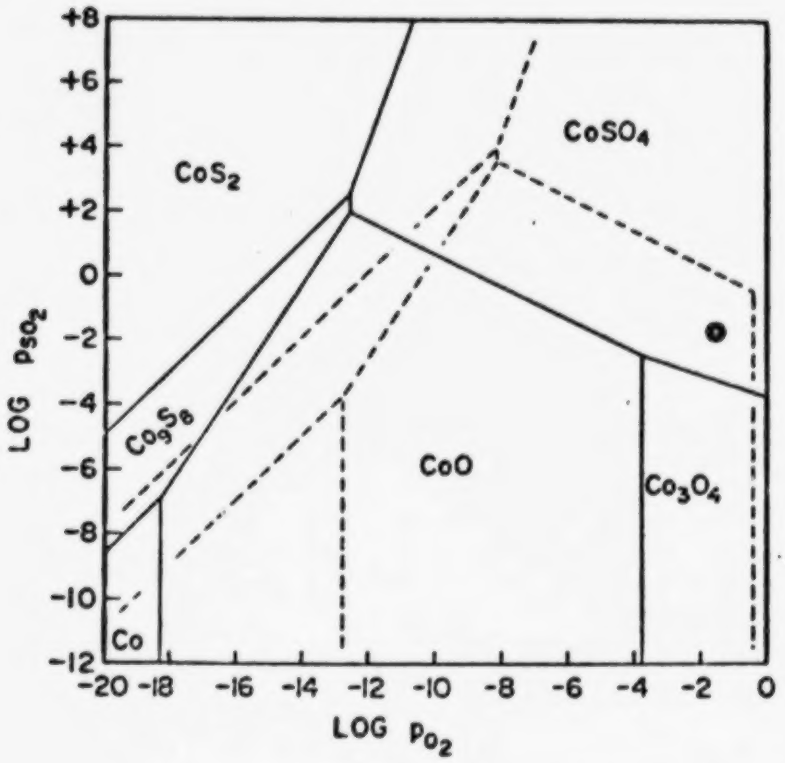
Figure 5 [36]


+10
+ 6
+ 2
- 2
- 6
-10
LOG p_{SO_2}
CuS
Cu_2S
Cu
Cu_2O
CuO
$CuO \cdot CuSO_4$
$CuSO_4$
+10
+ 6
+ 2
- 2
- 6
-10
-20 -16 -12 -8 -4 0
LOG p_{O_2}
12·5
11·5
10·5
$10^4 T$

Predominance-volume diagram showing volumes of stability occupied by various Cu-S-O compounds in the range of p_{SO_2} from 10^{-10} to 10^{10} atm, p_{O_2} from 1 to 10^{-20} atm, and temperature from 750° to 950°K.

T. R. Ingraham, "Thermodynamics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate", Trans. Met. Soc. AIME, vol. 233, pp. 359-67 (Feb. 1965).

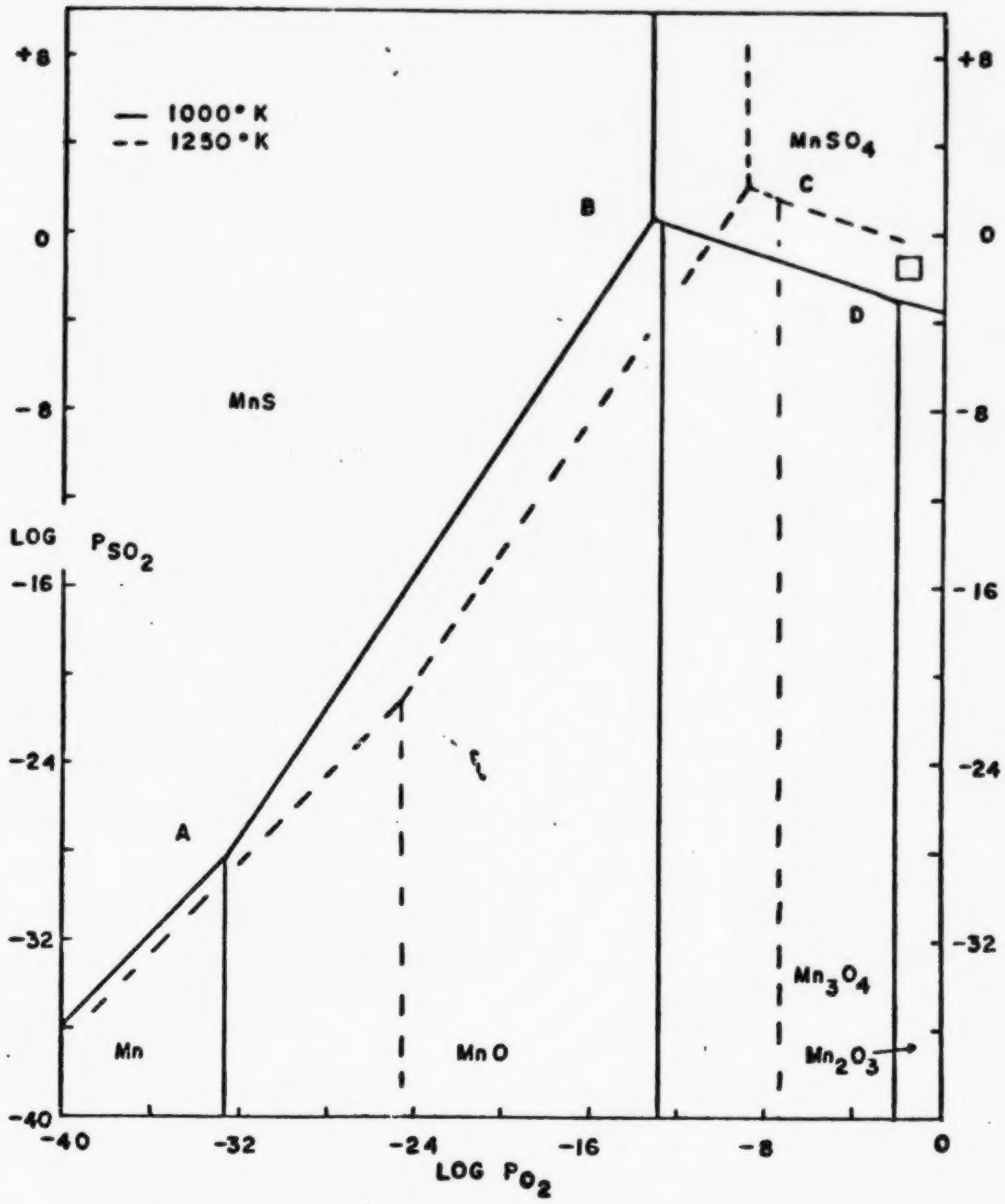
Figure 6 [39]



Predominance-area diagram showing the stable univariant equilibria and stable bivariant equilibria in Tables V and VI for temperatures of 950°K and 1200°K. Solid line 950°K, broken line 1200°K.

T. R. Ingraham, "Thermochemistry of the Co-S-O System from 950-1200° K", Can. Met. Quart., vol. 3, no. 3, pp. 220-34 (1964).

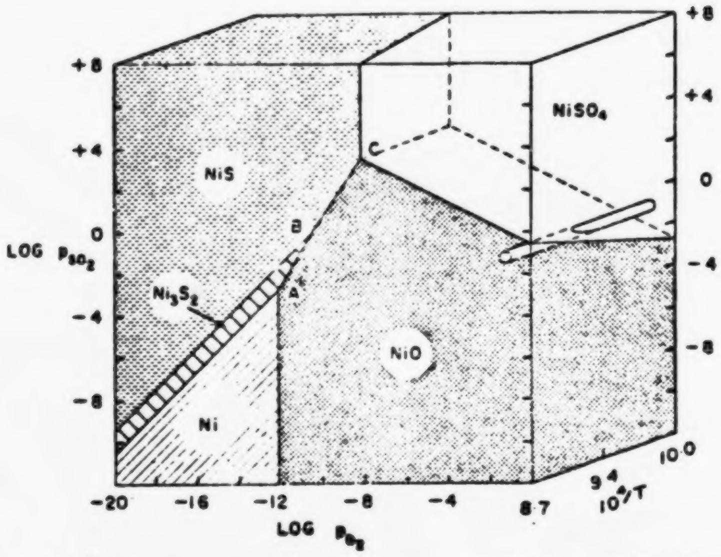
Figure 7 [37]



Logarithm p_{SO_2} versus logarithm p_{O_2} for the Mn-S-O system at 1000°K and 1250°K.

T. R. Ingraham, "Thermodynamics of the Mn-S-O System between 1000° and 1250° K", Can. Met. Quart., vol. 5, pp. 109-22 (1966).

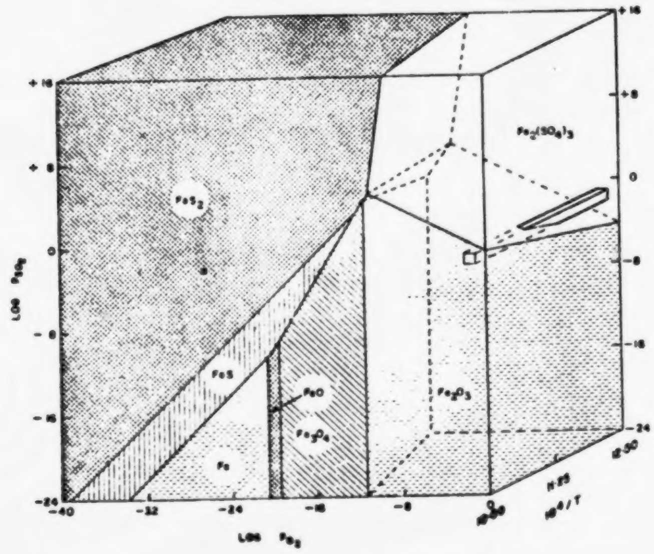
Figure 8 [40]



Predominance volume diagram for Ni-S-O system between 1000° and 1150° K.

T. R. Ingraham, "Thermodynamics of the Thermal Decomposition of Nickel (II) Sulfate: The Ni-S-O System from 1000° K to 1150° K", Trans. Met. Soc. AIME, vol. 236, no. 7, pp. 1064-7 (1966).

Figure 9 [38]



Predominance volume diagram for the iron-sulphur-oxygen system for the temperature range 800°-1000°K

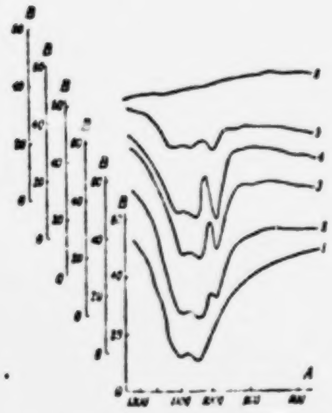
"Proceedings of the First International Meeting on Applications of Fundamental Thermodynamics to Metallurgical Processes", G. Fitterer, Ed., Gordon and Breach, New York, 1967.

As already mentioned, the reaction or decomposition products may be amorphous. This fact not only influences quantitative calorimetric measurements, but also complicates the identification of the end-products by x-ray techniques. The integral line breadth of an interference line is inversely proportional to the particle size. In extreme cases of small particle size, the maximum intensity of the line becomes very weak in comparison to the background intensity. [44]

In these cases the identification of reaction products is possible using IR-spectrophotometry. This method has been used by Guy Pannetier [42] and V. V. Pechkovskii [43]. The spectra of all the sulfates have a similiar structure due to the common ion $SO_4^=$. Difference in crystal structure and the difference in the mass of the cations however cause characteristic features for each individual compound.

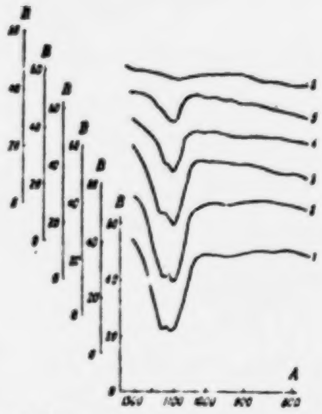
Figure 10 and 11 show two examples. Figure 10 shows a new maximum at 985 cm^{-1} beginning at about 700° C which has its greatest intensity in the spectrum of the products obtained at 800° C. Chemical analysis confirmed the formation of $CdO \cdot CdSO_4$[43]. (This result does not agree with the experiments of Guy Pannetier [25], who found for the basic sulfate the composition $2CdO \cdot CdSO_4$.) In the case of aluminum-sulfate no maximum occurs, indicating that the decomposition goes directly to the oxide [43].

Figure 10



Infrared spectra of the products of the thermal decomposition of $CdSO_4$ at various temperatures: 2) 700°; 3) 750°; 4) 800°; 5) 850°; 6) 900°. 1) Original material.

Figure 11



Infrared spectra of the products of the thermal decomposition of $Al_2(SO_4)_3$ at various temperatures: 2) 700°; 3) 750°; 4) 800°; 5) 850°; 6) 900°. 1) Original material.

V. V. Pechkovskii, M. S. Gaisinovich, "Infrared Spectra of Products of the Thermal Decomposition of Copper, Zinc, Cadmium and Aluminum Sulphates", Russ. J. Inorg. Chem., vol. 9, no. 10, pp. 1245-7 (Oct. 1964).

IV. OXIDES USED AS CATALYSTS IN SO_2-SO_3 OXIDATION

The following oxides act as catalysts in SO_2 oxidation: CuO[45], Fe_2O_3[45], Cr_2O_3-Al_2O_3[46], SnO_2-Cr_2O_3 (1.116:1 ratio)[47], V_2O_5-Fe_2O_3[48], Cr_2O_3[49], V_2O_5-Bi_2O_3[50], ZnO-V_2O_5[51], Alkali-sulfate-V_2O_5[52,53,54,55,56,57], Ba-Ni-Cr-Oxide [58], V_2O_5[59], B_2O_3-V_2O_5, MoO_3-V_2O_5, WO_3-V_2O_5[60], MoO_3[61], Fe_2O_3-MoO_3[62].

Some of the criteria which determine the usefulness of a catalyst are:

a) The oxidation rates should be high (low contact time).

b) At the working (ignition) temperature the equilibrium decomposition pressure of SO_3 of the corresponding sulfate must be higher than the SO_3 partial pressure in the gas phase. Otherwise a stable sulfate is formed and the catalyst becomes inactive.

For a V_2O_5 catalyst the ignition temperature is about 420° C. This temperature is about the same as the beginning decomposition temperatures for $V_2(SO_4)_3$ and $VOSO_4$ (see Table I). The use of mixtures of oxides as well as the addition of alkali-sulfates to the vanadium catalysts (formation of sulfovanadates $Me_2SO_4 \cdot V_2O_5$) seem to lower the ignition temperature or to act as promoters.

The aforementioned oxides might become important for our adsorption and regeneration process if they fullfill the following conditions (using V_2O_5 as an example):

Adsorption step:

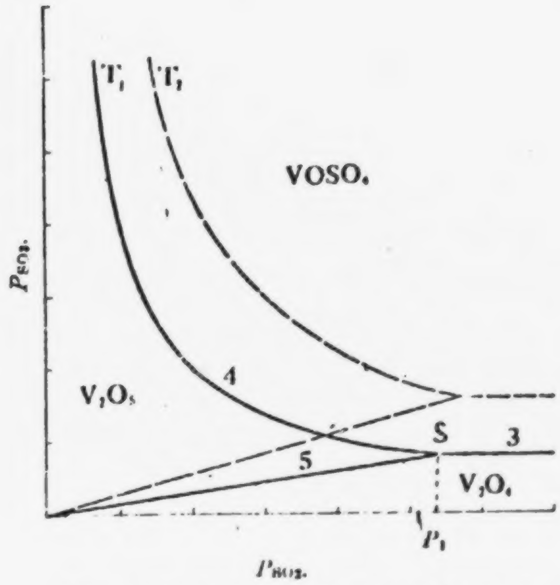
T_1: $2V_2O_5+2SO_2 \rightleftharpoons 2VOSO_4+V_2O_4$ ΔG negative
$T_1 <$ ignition temperature (sulfate formation)

Regeneration step:

T_2: $2VOSO_4 \rightarrow V_2O_4+2SO_3$ ΔG negative
T_2: $V_2O_4+\frac{1}{2}O_2 \rightarrow V_2O_5$ ΔG negative
with $T_1<T_2$
$T_2 >$ ignition temperature (sulfate decomposition)

H. Flood and O. J. Kleppa investigated the thermodynamically possible equalibria conditions for this example [63]. Figure 12 shows schematically the results. It is evident that there is, for a given SO_2 and SO_3 partial pressure, only one temperature at which all the solid phases are coexistent (univariant point). The area of stability of $VOSO_4$ depends on P_{SO_3}, P_{SO_2} and the temperature.

Figure 12



Conditions of existence of V_2O_4, V_2O_5 and $VOSO_4$ as functions of the partial pressure of SO_2 and SO_3.

The curves 3, 4 and 5 indicate the coexistence of two solid phases

N. Flood, O. J. Kleppa, "Investigations on the Equilibria in the System V_2O_4, V_2O_5, $VOSO_4$, SO_2, SO_3", J. Am. Chem. Soc., vol. 69, pp. 998-1002 (1947).

Quantitative phase diagrams like that shown in Figure 12 are of great help in determining the optimal working conditions. The prerequisits in constructing such diagrams are, naturally, exact knowledge of the decomposition path of the sulfates (existence of oxysulfates) and the thermodynamic properties of all compounds.

The decomposition behaviour of the corresponding sulfates of the above mentioned catalytically effective oxides is known (see Table I) with exception of molybdenum and tungsten-sulfate. Boron evidently forms no stable sulfate at all. It is evident that the catalysts mentioned in the literature are metals which can occur in different oxidation states, therefore, all metals like manganese, titanium, and cobalt which show the same behaviour deserve close consideration. Because of their importance these oxides and their reactions will be considered in greater detail in one of the next memoranda.

V. REDUCTIVE DECOMPOSITION OF SULFATES

The interaction of reducing compounds and sulfates is of technical importance in the reductive calcining of calcium sulfate, in converting insoluble barium sulfate into soluble bariumsulfide, and in other reactions in nonferrous metallurgy. The recent literature covering this subject is somewhat scarce. Reductive decomposition of sulfates formed when SO_2 is sorbed from flue gases on metal oxides is considered in some cases as a potential method for catalyst regeneration.

a) Reductive Decomposition of Calcium Sulfate

The reduction of calcium sulfate by carbon is described by A. Ginstling and A. D. Volkov [64].

The main reactions which take place are:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \tag{1}$$

and

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2 \tag{2}$$

These reactions are generally followed by side-reactions which lead to the formation of elemental sulfur. The reactions that were investigated were:

$$CaS+2SO_2 = CaSO_4+S_2 \qquad (3)$$

$$3CaS+CaSO_4 = 4CaO+2S_2 \qquad (4)$$

$$2CaS+SO_2 = 2CaO+1.5\ S_2 \qquad (5)$$

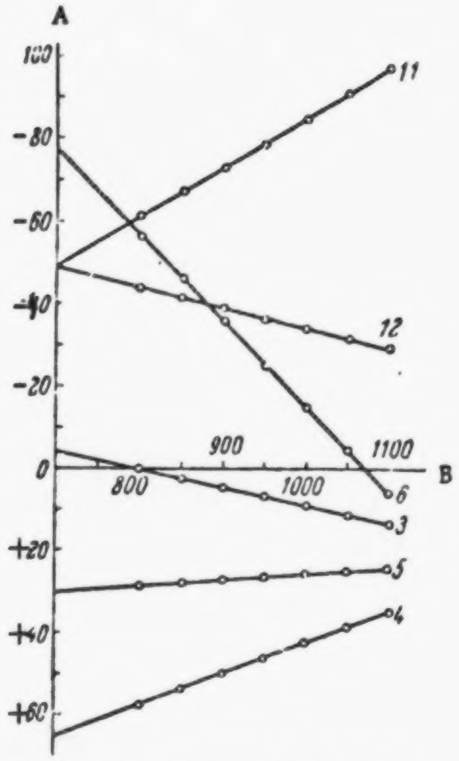
$$4CaO+6SO_2 = 4CaSO_4+S_2 \qquad (6)$$

$$2SO_2+4C = 4CO+S_2 \qquad (11)$$

$$2SO_2+4CO = 4CO_2+S_2 \qquad (12)$$

Ginstling and Volkov investigated the free energy change of these reactions as function of temperature. Figure 13 shows the results. It follows that at temperatures lower than 800° C, reaction (6) is the most important one in the production of S_2. At temperatures higher than 800° C reactions (11) and (12) are most important. In the absence of a reducing agent reactions (3) and (6) are responsible for sulfur formation. This result is important in connection with the simultaneous disproportionation and decomposition of sulfites. (see Technical Memorandum 004-009-CH3)

Figure 13

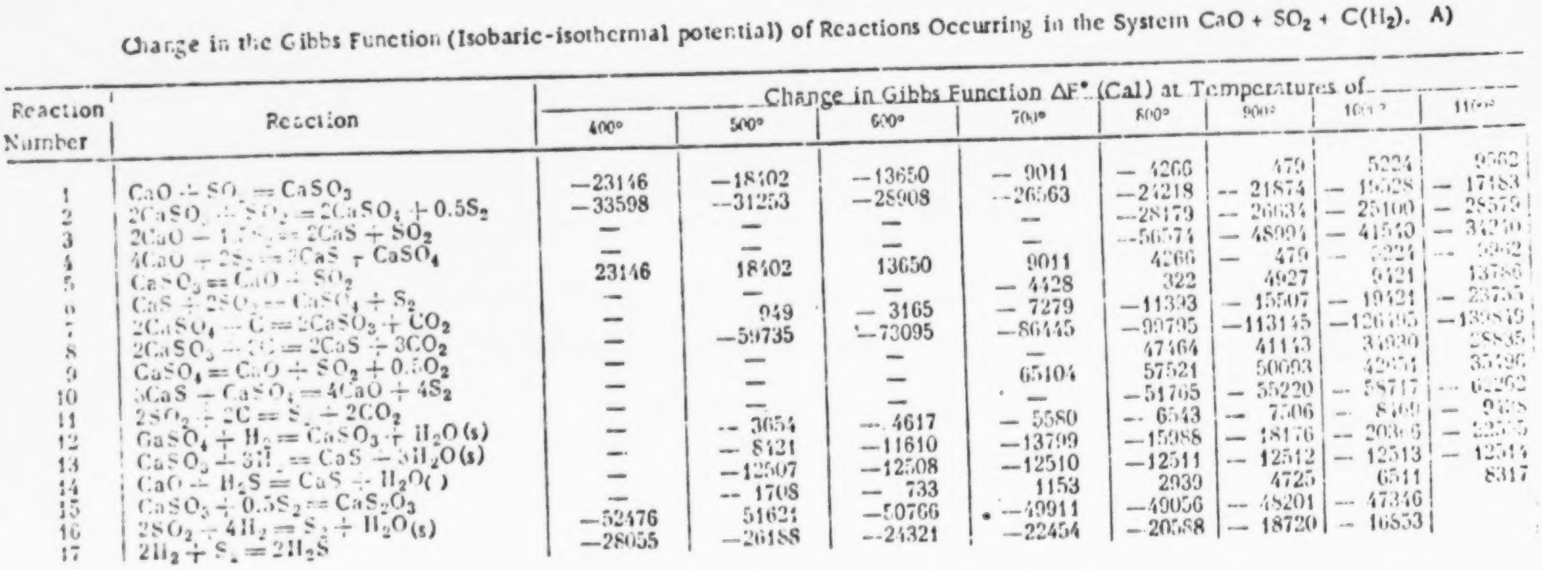


Free energy changes in the main reactions of sulfur formation in the system $CaSO_4$−C at various temperatures. A) Free energy change ΔZ_T° (kcal); B) temperature $\underline{t}$ (°C). The curve numbers correspond to the reaction numbers.

A. M. Ginstling, M. D. Volkov, "Reactions of Elemental Sulfur Formation in the Interaction of Calcium Sulfate with Carbon", Zhur. Prikl. Khim., vol. 33, no. 8, pp. 1700-4 (1960).

The secondary reactions are also investigated by V. V. Pechkovskii and T. G. Mal'tseva [65]. Table III shows the reactions investigated and the results. The thermodynamic calculations were checked with DTA experiments.

TABLE III



Change in the Gibbs Function (Isobaric-isothermal potential) of Reactions Occurring in the System $CaO + SO_2 + C(H_2)$. A)

Reaction Number	Reaction	Change in Gibbs Function ΔF° (Cal) at Temperatures of							
		400°	500°	600°	700°	800°	900°	1000°	1100°
1	$CaO + SO_2 = CaSO_3$	−23146	−18402	−13650	− 9011	− 4266	479	5224	9962
2	$2CaSO_3 + SO_2 = 2CaSO_4 + 0.5S_2$	−33598	−31253	−28908	−26563	−24218	− 21874	− 19528	− 17183
3	$2CaO + 1.5S_2 = 2CaS + SO_2$	—	—	—	—	−28179	− 26634	− 25100	− 28579
4	$4CaO + 2S_2 = 3CaS + CaSO_4$	—	—	—	—	−56574	− 48994	− 41540	− 34230
5	$CaSO_3 = CaO + SO_2$	23146	18402	13650	9011	4266	− 479	− 5224	− 9962
6	$CaS + 2SO_2 = CaSO_4 + S_2$	—	—	—	− 4428	322	4927	9421	13786
7	$2CaSO_4 + C = 2CaSO_3 + CO_2$	—	949	− 3165	− 7279	−11393	− 15507	− 19421	− 23755
8	$2CaSO_3 + 3C = 2CaS + 3CO_2$	—	−59735	−73095	−86445	−99795	−113145	−126495	−139849
9	$CaSO_4 = CaO + SO_2 + 0.5O_2$	—	—	—	—	47464	41143	34930	28835
10	$3CaS + CaSO_4 = 4CaO + 4S_2$	—	—	—	65104	57521	50093	42651	35496
11	$2SO_2 + 2C = S_2 + 2CO_2$	—	—	—	—	−51765	− 55220	− 58717	− 62262
12	$CaSO_4 + H_2 = CaSO_3 + H_2O(s)$	—	− 3654	− 4617	− 5580	− 6543	− 7506	− 8469	− 9455
13	$CaSO_3 + 3H_2 = CaS + 3H_2O(s)$	—	− 8421	−11610	−13799	−15988	− 18176	− 20366	− 22555
14	$CaO + H_2S = CaS + H_2O(\ )$	—	−12507	−12508	−12510	−12511	− 12512	− 12513	− 12514
15	$CaSO_3 + 0.5S_2 = CaS_2O_3$	—	− 1708	− 733	1153	2939	4725	6511	8317
16	$2SO_2 + 4H_2 = S_2 + H_2O(s)$	−52476	51621	−50766	−49911	−49056	− 48201	− 47346	
17	$2H_2 + S_2 = 2H_2S$	−28055	−26188	−24321	−22454	−20588	− 18720	− 16553	

V. V. Pechkovskii, T. Y. Mal'tseva, "The Interaction between Calcium Oxide and Sulfur Dioxide under Reducing Conditions", Zhur. Prikl. Khim., vol. 37, no. 2, pp. 240-6 (Feb. 1964).

The conclusions of Mal'tseva and Pechkovskii are the following:

1. From the experimental material obtained, it may be concluded that when calcium oxide reacts with sulfur dioxide in the presence of reducing agents in the low temperature region, calcium sulfate is formed through a sulfitization stage, while calcium sulfide is formed mainly by direct interaction between calcium oxide and the sulfur produced by reduction of sulfur dioxide. The formation of calcium sulfide is determined by the rate of the reduction of sulfur dioxide by the different reducing agents. At high temperatures, the formation of calcium sulfide is determined by the rate of reduction of calcium sulfate by various reducing agents.

2. From the thermographic analysis, it has been possible to show that the interaction of calcium with elemental sulfur occurs at a temperature of 455° C.

These results are in agreement with those obtained by Ginstling and Volkov.

b) Reductive Decomposition of Barium Sulfate

V. V. Pechkovskii and A. N. Ketov [66] found in their study that the reductive decomposition of Barium sulfate goes through the intermediate stage of sulfite formation. The following mechanism is presented:

$$2\ BaSO_3 \rightarrow 2\ BaO + 2\ SO_2$$

$$3\ SO_2 + 6\ CO \rightarrow 6\ CO_2 + 1.5\ S_2$$

$$2\ BaO + 1.5\ S_2 \rightarrow 2\ BaS + SO_2$$

$$BaSO_3 + 3\ CO \rightarrow BaS + 3\ CO_2$$

They found that $BaSO_3$ decomposes at 588° C both in a current of argon and in carbon monoxide. The reduction of Barium sulfate by carbon monoxide takes place at 772° C.

c) Reductive Decomposition of Iron, Manganese, Zinc, Mangnesium and Calcium-sulfate. [67]

In earlier publications the authors found that when the above mentioned sulfates were subjected to thermal decomposition, their stability increases as follows:

$$FeSO_4 < ZnSO_4 < MnSO_4 < MgSO_4 < CaSO_4$$

When these sulfates were roasted in the presence of carbon, the following results were found:

The solid end products from the reduction are the corresponding oxides and sulfides. The relative amounts vary widely depending on the amount of carbon and the roasting temperature.

In the presence of carbon the decomposition temperatures are about 100° C lower than in the thermal decomposition (450° C for $FeSO_4$ and 650° C for $MnSO_4$).

When the amount of carbon does not exceed 5-10%, the principal solid products of the thermochemical decomposition of the sulfates of iron and manganese are the corresponding oxides. In this case the sulfur in the gas phase exists mainly as SO_2.

When the amount of carbon is above 10-15%, the end products also contain the corresponding sulfides.

In order to obtain the oxides the amount of carbon in the batch should be as low as necessary for reduction and the temperature should not exceed 700-750° C.

In order to obtain large amounts of sulfides, the process must be run at higher temperatures and with a large amount of carbon in the starting batch. Tables IV-IX show the quantitative results of Pechkovskii.

TABLE IV

Degree of Thermochemical Conversion of Ferrous Sulfate as a Function of the Temperature and Amount of Carbon in the Mixture.

Amount of carbon in mixture (in %)	Degree of $FeSO_4$ conversion (in %)						
	450°	500°	550°	600°	650°	700°	750°
0.0	0.0	0.8	4.7	25.4	66.6	92.7	99.6
5.0	0.9	7.2	40.6	84.3	95.0	98.2	99.8
10.0	2.3	15.1	70.0	93.7	98.8	99.1	99.4
20.0	4.6	21.9	75.1	96.6	99.3	99.4	99.7

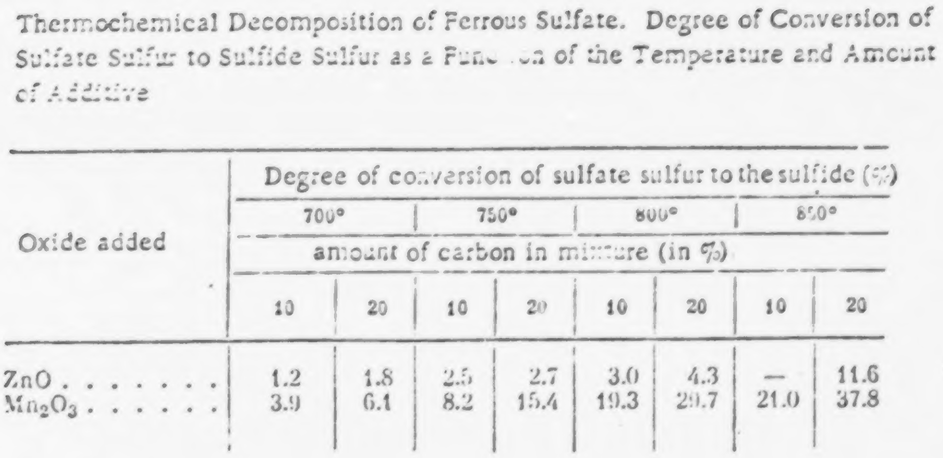
TABLE V

Thermochemical Decomposition of Ferrous Sulfate. Degree of Conversion of Sulfate Sulfur as a Function of the Temperature and Amount of Carbon in the Mixture

Amount of carbon in mixture (in %)	Degree of conversion of sulfate sulfur (in %)						
	750°		800°		850°		900°
	sulfide	pyrrhotite	sulfide	pyrrhotite	sulfide	pyrrhotite	sulfide
10.0	0.8	3.5	2.1	4.8	6.7	7.2	11.4
20.0	1.3	6.7	8.4	5.6	10.3	15.1	23.1
30.0	3.4	10.6	12.1	24.3	21.2	—	—

V. V. Pechkovskii, "Rules for the Formation of Sulfides and Oxides of Metals in the Thermochemical Decomposition of the Sulfates of Manganese and Iron", J. Appl. Chem. USSR, vol. 32, pp. 2691-6 (1959).

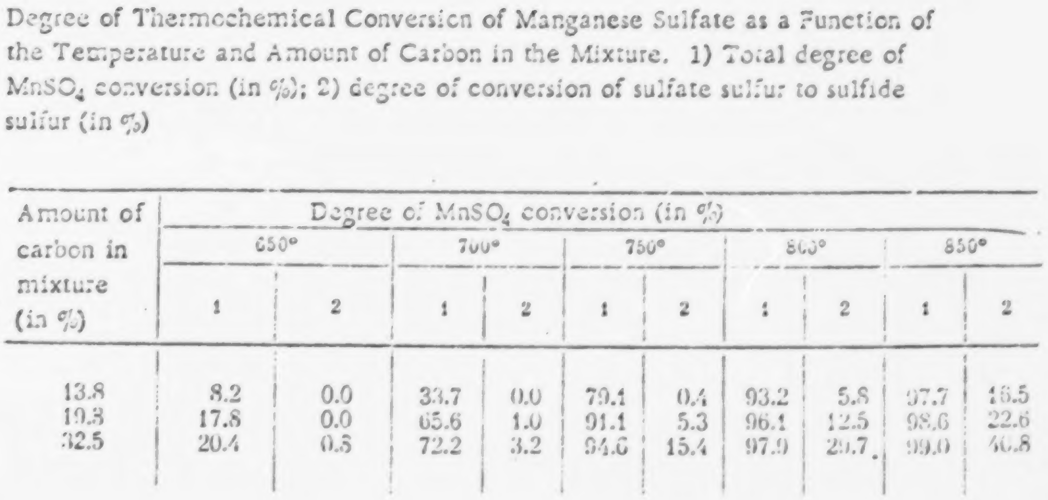
TABLE VI



Thermochemical Decomposition of Ferrous Sulfate. Degree of Conversion of Sulfate Sulfur to Sulfide Sulfur as a Function of the Temperature and Amount of Additive

Oxide added	Degree of conversion of sulfate sulfur to the sulfide (%)							
	700°		750°		800°		850°	
	amount of carbon in mixture (in %)							
	10	20	10	20	10	20	10	20
ZnO	1.2	1.8	2.5	2.7	3.0	4.3	—	11.6
Mn_2O_3	3.9	6.1	8.2	15.4	19.3	29.7	21.0	37.8

TABLE VII



Degree of Thermochemical Conversion of Manganese Sulfate as a Function of the Temperature and Amount of Carbon in the Mixture. 1) Total degree of $MnSO_4$ conversion (in %); 2) degree of conversion of sulfate sulfur to sulfide sulfur (in %)

Amount of carbon in mixture (in %)	Degree of $MnSO_4$ conversion (in %)									
	650°		700°		750°		800°		850°	
	1	2	1	2	1	2	1	2	1	2
13.8	8.2	0.0	33.7	0.0	79.1	0.4	93.2	5.8	97.7	16.5
19.3	17.8	0.0	65.6	1.0	91.1	5.3	96.1	12.5	98.6	22.6
32.5	20.4	0.5	72.2	3.2	94.6	15.4	97.9	29.7	99.0	40.8

V. V. Pechkovskii, "Rules for the Formation of Sulfides and Oxides of Metals in the Thermochemical Decomposition of the Sulfates of Manganese and Iron", J. Appl. Chem. USSR, vol. 32, pp. 2691-6 (1959).

TABLE VIII

Thermochemical Decomposition of Manganese Sulfate. Degree of Conversion of Sulfate Sulfur to Sulfide Sulfur as a Function of the Temperature and Amount of Additive (Amount of carbon in mixture = 24.2%)

	Degree of conversion of sulfate sulfur to the sulfide (in %)				
	700°	750°	800°	850°	900°
Without additive. . . .	1.8	10.3	21.5	31.6	35.5
Without additive* . . .	2.0	31.1	59.1	82.0	87.5
Additive:					
CaO	8.9	27.0	37.5	60.1	71.7
Mn_2O_3	26.7	57.4	64.1	70.8	72.3

---

*In a stream of argon containing 7.5% SO_2.

TABLE IX

Thermochemical Decomposition of Magnesium, Iron, Manganese, Zinc and Calcium Sulfates. Degree of Conversion of Sulfate Sulfur to the Sulfide as a Function of the Temperature (Amount of carbon in mixture = 28.0%)

Sulfate	Degree of conversion of sulfate sulfur to the sulfide (in %)					
	700°	750°	800°	850°	900°	950°
$MgSO_4$	0.1	0.	0.2	0.1	0.3	0.3
$FeSO_4$	0.4	2.5	10.8	19.3	25.6	—
$MnSO_4$	2.2	12.1	26.7	37.5	39.0	48.8
$ZnSO_4$	10.4	22.3	34.4	43.3	50.1	53.3
$CaSO_4$	0.0	1.1	3.6	15.2	50.0	87.7

V. V. Pechkovskii, "Rules for the Formation of Sulfides and Oxides of Metals in the Thermochemical Decomposition of the Sulfates of Manganese and Iron", J. Appl. Chem. USSR, vol. 32, pp. 2691-6 (1959).

These results agree well with the thermodynamic investigation of Ginstling and Volkov (see Part 4a). In the presence of large amounts of reducing agent the equilibria in equation (11) and (12) are strongly shifted to the right. A large amount of S_2 is formed. As a consequence equations (4) and (5) are shifted to the left. The oxide is transformed into sulfide. The observed temperature dependency shows the same tendency for $CaSO_4$ (see Figure 13). The free energy change of equation (11) becomes increasingly negative.

VI. SUMMARY

Based on their decomposition behaviour, the sulfates can be divided into four groups. The first group shows a simple decomposition to the corresponding oxides and SO_3. The second group decomposes to oxysulfates as an intermediate and finally to the oxide. The third group decomposes with an oxidation of the cation. The fourth group decomposes with reduction of the cation.

The first group contains the sulfates of the alkali and alkaline earth metals and the sulfates of Sc, Zn, Hf, Al, and Ga. Most of the transition metals belong to Group 2 and 3.

The fourth group comprises the noble elements (Ag and Pd). The sulfates decompose forming the elements.

The thermodynamic functions are known for only a few oxysulfates. The most accurate (but time consuming) experimental technique to determine these unknown values seems to be the static vapor-pressure-measurement with the apparatus described by Ingraham. Other helpful methods are DTA, TGA, GA, and X-Ray. In the case of amorphous end products IR-techniques are useful. With these methods seven predominance area diagrams for Me-S-O systems have established in recent years. With these diagrams the thermodynamically favored compounds may be predicted for a given temperature and given P_{SO_2} and P_{O_2} partial pressures.

The sulfates can be divided into two groups according to the temperature ranges of the sulfate decomposition. The following sulfates decompose at temperatures higher than 800° C. Alkaline and alkaline earth-sulfates (with Be as exception) and the sulfates of Th,La, Mn, Co, Ni, Cu, Ag, Cd, Pb, and Bi.

Under 800° C the following sulfates can be decomposed thermally: Bi, Ti, Zr, Hf, V, Cr, Fe, Zn, Al, Ga, Sc, Sn, and Ce.

The fact that a sulfate may be decomposed is usually a consequence of a small free energy change upon formation of the sulfate. Most of the transition metals may be thermally decomposed. Hence many of the transition metals seem useful for our purpose.

Many corresponding oxides are known to be capable of oxidizing SO_2 to SO_3 (catalysts). These oxides should be considered closely, as they probably will have good kinetic qualities.

The reductive decomposition of sulfates shows the following regularities: The composition of the end product depends upon the reaction temperature and the reductive agent to sulfate ratio. At high temperatures and high ratios the end products are the corresponding oxides and sulfides. At low temperatures and low ratios the end products are the corresponding oxides only. This information should be useful in regeneration schemes.

TABLE I

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
Li_2SO_4	T >860° C: $Li_2SO_4 \rightarrow Li_2O+SO_2+\frac{1}{2}O_2$	[1]	Melting point 860° C.
		[2]	Anhydrous form is stable between 150-770° C and can be used in this range as an analytical standard. Tests have been run in open crucibles at 300° /hr.
Na_2SO_4	T > 900° C: $Na_2SO_4 \rightarrow Na_2O+SO_2+\frac{1}{2}O_2$	[1]	Weight loss when held for 2 hours at 1200° C was 1.05%.
		[3]	Sodium sulfate decomposes faster in the presence of V_2O_5. Decomposition is fast enough for convenient measurement at temperatures >600° C. Depending on the ratio of oxide to sulfate, the rate can get 10 times faster.
K_2SO_4	T >900° C $K_2SO_4 \rightarrow K_2O+SO_2+\frac{1}{2}O_2$	[1]	Reaction is accompanied by sublimation of K_2SO_4. Weight loss when held for 2 hours at 1200° C was 3.6%. Discrepancies in the literature.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
Rb_2SO_4	T >900° C: $Rb_2SO_4 \rightarrow Rb_2O+SO_2+\frac{1}{2}O_2$	[1]	Reaction is accompanied by sublimation of Rb_2SO_4. Weight loss when held for 2 hours at 1200° C was 6.3%.
Cs_2SO_4	T >1036° C: $Cs_2SO_4 \rightarrow Cs_2O+SO_2+\frac{1}{2}O_2$	[1]	Reaction is accompanied by sublimation. Melting point 1036° C. Weight loss when held for 2 hours at 1200° C was 13.9%.
$BeSO_4$	T = 690-760° C: $BeSO_4 \rightarrow BeO+SO_2+\frac{1}{2}O_2$	[4]	The value 690° C was found by mass spectrometric thermal analysis (MTA). The value of 760° C was determined in a DTA experiment. The intermediate basic salt 5 BeO · SO_3 reported by Marchal was not confirmed by other investigators [1].
$MgSO_4$	T ≥950, 871° C: $MgSO_4 \rightarrow MgO+SO_2+\frac{1}{2}O_2$	[1]	T ≥ 950° C static method T ≥ 871° C dynamic method
		[5]	W. E. Brownell gives T >900° C as decomposition temperature.
		[6]	A. Kh. Bronnikov gives T = 1120-50° C as

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
			temperature range where intense decomposition occurs. In the presence of SiO_2 (0.5 mole per mole $MgSO_4$) decomposition of $MgSO_4$ increases remarkably in the range 1000-1200° C, accompanied by decomposition formation of Mg-silicate.
		[7]	V. V. Pechkovskii et al. investigated the kinetics. Decomposition is reported to be a linear function of time between 1020-60° C. Addition of 5% CuO, Fe_2O_3 or Cr_2O_3 caused a higher decomposition rate.
$CaSO_4$	T >1227-1527° C: $CaSO_4 \rightarrow CaO+SO_2+\frac{1}{2}O_2$	[1]	CaO forms a eutectic with $CaSO_4$ near 1365° C.
		[5]	In the presence of SiO_2 there is a reaction between $CaSO_4$ and SiO_2 prior to decomposition of $CaSO_4$, with evolution of SO_2.
		[8]	Dissociation rate of $CaSO_4$ is influenced by the presence of Al_2O_3, SiO_2 and Fe_2O_3.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
		[9]	The effect of additives (Fe_2O_3, soda, CaF_2, borax) on the rate of decomposition of $CaSO_4$ in a mixture with silica, alumina, and kaolin was studied. The best accelerating additives were borax (0.5%) and Na_2SO_4 ($\leq 3\%$ of charge weight). The accelerating effect of Na_2SO_4 is explained by the appearance of centers of a liquid microphase.
$SrSO_4$	T = 1374° C: $SrSO_4 \rightarrow SrO + SO_2 + \frac{1}{2}O_2$	[1]	The decomposition temperatures reported by different investigators are in disagreement.
$BaSO_4$	T >1347° C: $BaSO_4 \rightarrow BaO + SO_2 + \frac{1}{2}O_2$	[1]	Melts without obvious decomposition. Melting point: 1347° C.
$Sc_2(SO_4)_3$	T = 780° C: $Sc_2(SO_4)_3 \rightarrow Sc_2O_3 + 3SO_2 + {}^3/_2 O_2$	[1]	Seems to decompose directly to oxide unlike other rare-earth sulfates. With exception of $Ce_2(SO_4)_3$, it is the least stable rare-earth sulfate.

TABLE I
Page 5

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Y_2(SO_4)_3$	T = 920° C: $Y_2(SO_4)_3 \rightarrow Y_2O_2(SO_4)+2SO_2+O_2$ T = 1124° C: $Y_2O_2(SO_4) \rightarrow Y_2O_3+SO_2+\frac{1}{2}O_2$	[10]	The formation of the basic salts occurs for the rare-earth sulfates rapidly between 855-946° C. The minimum decomposition temperature for the basic sulfates is 1090-1250° C. Experiments were done with DTA in a dynamic atmosphere of argon under atmospheric pressure.
$La_2(SO_4)_3$	T = 890° C: $La_2(SO_4)_3 \rightarrow La_2O_2 \cdot SO_4+2SO_2+O_2$ T >1096° C: $La_2O_2SO_4 \rightarrow La_2O_3+SO_2+\frac{1}{2}O_2$	[10]	See $Y_2(SO_4)_3$
		[11]	$La_2O_2(SO_4)$ belongs to the tetragonal system with a = 6.88 and C = 12.30 Å. Decomposition occurs between 770 and 1320° C.
		[12]	The stability of the rare-earth oxysulfates decreases in the following order: La, Pr, Nd, Sm, Gd, Eu, Y, Yb, which is the order of increasing at. no. with the exception of the Gd-Eu reversal. Essentially these same results are reported by Wendlandt and Nathans [10].

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Ce_2(SO_4)_3$	T >650° C: $Ce_2(SO_4)_3 \rightarrow$ anhydrous salt+$SO_3 \rightarrow CeO_2$	[1] [13]	CeO_2 is the end product when experiments are performed in air. The mechanism is unknown.
$Ce(SO_4)_2 \cdot 4H_2O$	Up to 400° C: loss of $4H_2O$ Up to 860° C: loss of O_2 and formation of $Ce(SO_3)_2$ >860° C decomposition of sulfite; end product CeO_2	[14]	Béla Lóránt used thermo-balance. The formation of $Ce(SO_3)_2$ was postulated only by stoichiometric calculations and comparison with weight loss. In addition he worked with a covered crucible. The atmosphere was therefore not well defined.
$Ti(SO_4)_2$	T >150° C: $Ti(SO_4)_2 \rightarrow TiOSO_4$ T >430° C $TiOSO_4 \rightarrow TiO_2$	[1]	Decomposition is complete at about 600° C. Experiments by Chuklantsev were done in dry argon. $TiSO_4$: uncertain existence $Ti_2(SO_4)_3$: Thermal properties unknown except that it yields TiO_2 on ignition.
$Zr(SO_4)_2$	T = 576-632° C Decomposition goes directly to ZrO_2	[1]	

TABLE I
Page 7

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$[ZrO(OH)]_2 \cdot SO_4$	T = 315° C: Formation of ZrO_2 and $ZrOSO_4$ T = 565-780° C: Decomposition of $ZrOSO_4$	[15]	
$Hf(SO_4)_2$	T = 550-650° C: $Hf(SO_4)_2 \rightarrow HfO_2$	[1]	Decomposition goes directly to HfO_2. No intermediate compound was found. $Hf(SO_4)_2$ appears to be more stable than $Zr(SO_4)_2$.
$V_2(SO_4)_3$	T >380° C: $V_2(SO_4)_3 \rightarrow V_2O_5$ T >408° C: $V_2(SO_4)_3 \rightarrow$ mixture of V_2O_4 and V_2O_5	[1]	Experiment was performed in vacuo.
$VOSO_4$	$T \approx 400°$ C: $VOSO_4 \rightarrow V_2O_5$, SO_3, and SO_2	[1]	When heated in vacuo the total pressure reaches 2 Atm. at 610° C. The equilibrium partial pressure of SO_3 is about 1 Atm. at this temperature.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$V_2O_5 \cdot 2SO_3$ $V_2O_5 \cdot 3SO_3$ $V_2O_5 \cdot 4SO_3$	T = 100-200° C: Decomposition	[1]	
$Cr_2(SO_4)_3 \cdot 18H_2O$	Up to 450° C: Loss of 16 moles water. T = 460-640° C: Loss of the remaining 2 moles of water and formation of a basic salt $Cr_2(SO_4)_3 \rightarrow SO_3 + Cr_2O(SO_4)_2$	[14]	See remark under Ce.
$MnSO_4 \cdot 5H_2O$	$T \approx 380°$ C: $2MnSO_4 + O \rightarrow Mn_2O(SO_4)_2$ 720° C and 880° C maxima in DTA plot. No weight change in TGA experiment. T >880° C loss of SO_3 Decomposition is complete at 1090-1100° C. End product is Mn_3O_4	[14]	Another basic salt ($MnOSO_4$) mentioned in the literature did not fit into the DTA plots of Béla Lóránt.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
Mn III-Sulfate	T <950° C (air): Decomposition product Mn_2O_3 ; T >950° C (air): Decomposition product Mn_3O_4 ; Any Mn_2O_3 formed changes to Mn_3O_4 at 950° C; In N_2 decomposition product is MnO	[16]	
$FeSO_4 \cdot 7H_2O$	Up to 520-530° C: All water of hydration is lost. T = 520-530° C oxidation begins: $2FeSO_4 + \frac{1}{2}O_2 \rightarrow Fe_2O(SO_4)_2$ T >800° C: $Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3$	[14]	See remark under Ce. The intermediate oxysalt was not confirmed by other investigators.
$Fe_2(SO_4)_3 \cdot 5H_2O$	Up to 320° C: loss of 5 moles H_2O T = 650-800° C:	[14]	See remark under Ce.

TABLE I
Page 10

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERA-TURE	REMARKS
	$Fe_2(SO_4)_3 \rightarrow Fe_2O_2(SO_4)+2SO_3$ $Fe_2O_2(SO_4) \rightarrow Fe_2O_3+SO_3$		
$FeSO_4$	T = 700-720° C (2 hrs.): $FeSO_4 \rightarrow$ red Fe oxide	[17]	Iron sulfate was calcinated in a fluidized bed (pilot plant experiments). At this temperature decomposition takes place at a satisfactory rate.
$FeSO_4 \cdot 7H_2O$	T >450° C: $2[FeSO_4 \cdot 7H_2O] \rightarrow Fe_2O_3+SO_2+SO_3+14H_2O$	[18]	
$Fe_2(SO_4)_3$	T >700° C $Fe_2(SO_4)_3 \rightarrow Fe_2O_3+SO_3$	[1]	Decomposition is reversible without the formation of intermediate compounds. According to [1] $FeSO_4$ decomposes irreversibly with oxidation to Fe_2O_3. The intermediates have not been identified with certainty.

TABLE I
Page 11

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Fe_5(OH)_{13}SO_4$	T = 80-280° C: Dehydration; T = 350-450° C: Solid-solid transition; T = 690° C: Decomposition of the hydroxy into the oxysalts.	[15]	
$Fe(SO_4)\cdot xH_3O$	T = 318-40° C: Dehydration of $FeSO_4 \cdot xH_2O$; T = 603-753° C: Oxidation of $FeSO_4$ to $Fe_2(SO_4)_3$ T = 781-810° C: Decomposition of $Fe_2(SO_4)_3$ There are two endothermic transformations. One is between 881 and 888° C. The other is between 956 and 948° C. They are made without change in wt. Their nature is unknown.	[19]	Results were obtained in an Ar atmosphere

	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$FeSO_4 \cdot 7H_2O$	Decomposition includes the following steps: Heptahydrate → Tetrahydrate → Monohydrate → Anhydrous. Salt → $Fe_2O_3 + SO_2$	[20]	Experiments were made in an inert atmosphere The results are about the same in an oxidizing atmosphere.
$CoSO_4 \cdot 7H_2O$	T = 300-420° C: loss of the 7 moles H_2O T = 420° C oxidation: $2CoSO_4 + \frac{1}{2}O_2 \rightarrow Co_2O(SO_4)_2$ T = 900-1000° C: $Co_2O(SO_4)_2 \rightarrow Co_2OSO_4 + SO_3 + \frac{1}{2}O_2$ finally → Co_3O_4.	[14]	See remark under Ce.
	In vacuo the decomposition product is CoO.	[1]	Pechkovskii found no evidence of an oxysulfate. SO_2 in the carrier gas inhibits the decomposition. Investigation temperatures ranged 750-950° C.
	T > 782° C: $CoSO_4 \rightarrow CoO + SO_3$ T < 782° C: A mixture of CoO and Co_3O_4 is found	[21]	In a static experiment T. R. Ingraham also found no evidence for the basic sulfate mentioned by Lóránt.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$NiSO_4 \cdot 6H_2O$	Up to 485° C loss of water of hydration. T >800° C: Decomposition forming a mixture of NiO and Ni_2O_3.	[14]	See remark under Ce.
		[1]	Marchal, Wöhler and Flick investigated $NiSO_4$ in the range 700-945° C and 775-846° C respectively in a static system. No evidence of an oxysulfate.
$PdSO_4 \cdot 2H_2O$	The hydrate on heating loses first H_2O, then SO_2, yielding ultimately the metal.	[1]	No temperatures and no original literature given.
Cu_2SO_4	Cu_2SO_4 oxidizes in air.	[1]	No temperature and no original literature given.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$CuSO_4$	780-860° C formation of $CuO \cdot CuSO_4$; Then decomposition yielding CuO.	[1]	The rate of decomposition decreases with increasing oxygen content in the gas phase. Ferric and chromic oxides increase the decomposition rate.
$CuSO_4 \cdot 5H_2O$	Up to 360° C water of hydration lost. T = 700-840° C: $2CuSO_4 \rightarrow SO_3 + CuO \cdot CuSO_4$ T = 840-935° C: $CuO \cdot CuSO_4 \rightarrow CuO + SO_3$	[14]	See remark under Ce.
$CuSO_4$	T = 760° C: Basic sulfate is formed.	[7]	
$CuSO_4$	T >590° C: $2CuSO_4 \rightarrow CuO \cdot CuSO_4 + SO_3$ T >700° C: $CuO \cdot CuSO_4 \rightarrow 2CuO + SO_3$	[22]	Experiments performed in air and steam. Decomposition products were investigated chemically and by x-ray diffraction.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$CuSO_4$	T = 650° C: formation of $CuO \cdot CuSO_4$	[23]	Experiments performed in a stream of N_2.
Ag_2SO_4	Decomposes above its melting point. Using TGA it has appeared stable to 790° C. Decomposition yields the metal.	[1]	Marchal gives 104 mm Hg as the equilibrium pressure at 1130° C.
	T >840° C: $Ag_2SO_4 \rightarrow Ag_2SO_3 + O$ $Ag_2SO_3 \rightarrow Ag_2O + SO_2$ $Ag_2O \rightarrow 2Ag + O$	[14]	Melting point of salt is 680° C. See remark under Ce.
$ZnSO_4$		[1]	The formula $2ZnO \cdot 3ZnSO_4$ given for the oxysulfate was shown to be wrong [24, 23, 22].
	T >610° C: $3ZnSO_4 \rightarrow ZnO \cdot 2ZnSO_4 + SO_3$ T >740° C: $ZnO \cdot 2ZnSO_4 \rightarrow 3ZnO + 2SO_3$	[22]	Experiment was performed in air.

COMPOUNDS	REACTION AND REACTION TEMPERATURES	LITERATURE	REMARKS
$CdSO_4 \cdot {}^8/_3 H_2O$	T = 115-141° C: $CdSO_4 \cdot {}^8/_3\ H_2O \rightarrow CdSO_4 \cdot H_2O + {}^5/_3\ H_2O$ T = 202° C: $CdSO_4 \cdot H_2O \rightarrow CdSO_4 + H_2O$ T = 807-825° C: $\alpha\ CdSO_4 \rightarrow \beta\ CdSO_4$ T = 853-870: $3\gamma CdSO_4 \rightarrow CdSO_4 \cdot 2CdO + 2SO_3$ T = 1036-1065° C: $CdSO_4$ melts T >1065° C: $CdSO_4 \cdot 2CdO \rightarrow 3CdO + SO_3$	[25]	Investigations were performed under a stream of nitrogen. X-ray data for $CdSO_4 \cdot 2CdO$ have been established.
$Al_2(SO_4)_3$	T = 650-950° C: $Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_2 + {}^3/_2 O_2$	[1]	Decomposition goes directly to oxide. No intermediate compound has been reported. In a patent of the North American Coal Corp. [26] $Al_2(SO_4)_3$ is decomposed at 800° C to give Al_2O_3 and a mixture of SO_3 and SO_2. The decomposition rate was found to be independent of flow rate of an inert gas. Starting with $Al_2(OH)_4SO_4$, N. N. Mitonov reports the formation of $AlOSO_4$ at a temperature of about 350° C.

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Ga_2(SO_4)_3$	T = 560-700° C: $Ga_2(SO_4)_3 \rightarrow Ga_2O_3 + 3SO_3$	[1]	From vapor pressure comparisons, $Ga_2(SO_4)_3$ appears to be less stable than $Al_2(SO_4)_3$.
$Ga_4(OH)_{10}SO_4$	T = 480-520° C: Water of hydration is lost and $GaOSO_4$ formed. T = 570° C: Solid-solid transition. T = 850-900° C: SO_3 is lost	[15]	
$SnSO_4$	T >360° C: Even in N_2 self oxidation $SnSO_4 \rightarrow SnO_2 + SO_2$; reaction rate increases between 350-400° C. Under continuous evacuation (heating rate 100°/hr): 320° C: beginning of decomposition. 597° C: decomposition complete.	[1]	No oxysulfate was formed.

	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Sn(SO_4)_2$	Is reported to become unstable not far above 100° C. However, using TGA in vacuum (heating rate [90° C/hr] up to 300° C, then [150° /hr]) decomposition was noticeable at 300° C with complete conversion to SnO_2 by about 587° C.	[1]	The anhydrous $Sn(SO_4)_2$ is very hygroscopic.
$PbSO_4$	Kellogg and Basu report basic sulfates. Temperature of stability depends on partial pressure of SO_2. $P_{SO_2} = 10^{-2}$ Atm. $T \approx 552° C$: $PbSO_4 \rightarrow PbO \cdot PbSO_4$ $T \approx 687° C$: $\rightarrow PbSO_4 \cdot 2PbO$ $T \approx 707° C$: $\rightarrow PbSO_4 \cdot 4PbO$ $T \approx 800° C$: $PbSO_4 \cdot 4PbO \rightarrow PbO$	[27]	

COMPOUND	REACTION AND REACTION TEMPERATURE	LITERATURE	REMARKS
$Bi_2(SO_4)_3$	Stable up to 380° C $T \geq 425°C$: $\rightarrow Bi_2O_3 \cdot 2Bi_2(SO_4)_3$. $T \geq 555°C$: $\rightarrow (2Bi_2O_3) \cdot Bi_2(SO_4)_3$. $T \geq 620°C$: $\rightarrow (3Bi_2O_3) \cdot Bi_2(SO_4)_3$. $T \geq 860°C$: $\rightarrow Bi_2O_3$	[28]	Results are based on studies by thermogravimetric and thermographic methods combined with chemical analysis of the products.
$U(SO_4)_2$	$T \approx 297°C$ Formation of $UO_2 \cdot SO_4$ even in the absence of air.	[1]	The existence of an anhydrous $U(SO_4)_2$ is not certain.
UO_2SO_4	$T > 500°C$ Decomposition to oxides with various stoichiometry, varying between the limits UO_3 and UO_2.	[1]	
$Th(SO_4)_2$	Stable to at least 400° C $T > 800°C$ Decomposition to ThO_2	[1]	At 723° C $P_{SO_3} = 1.56 \times 10^{-3}$ [Atm]. Decomposition is reported to go through an oxysulfate intermediate.

LITERATURE

(1) U. S. Department of Commerce, National Bureau of Standards: "High Temperature Properties and Decomposition of Inorganic Salts. (Part 1, Sulfates)." NSRDS-NBS7, Issued October 1, 1966.

(2) Clement Duval (Lab. Rech. Micro-Anal., Paris): "Thermal Stability of Analytical Standards." Microchim. Ichnoanal. Acta 1964(6), 1073-81 (Fr). C.A., 62:5877 c.

(3) I. R. Polyvyannyi and V. G. Avrov: "The Kinetics of the Thermal Decomposition of Sodium Sulfate in the Presence of Vanadium Pentoxide." Tr. Inst. Met. I. Obogashch., Akad. Nauk Kaz. SSR 5, 41-48 (1962). C.A., 58, 10773 d.

(4) H. G. Langer and R. S. Gohlke: "Mass Spectrometric Thermal Analysis (MTA)." Anal. Chem. 35 (9), 1301-2 (1963).

(5) W. E. Brownell (Alfred Univ., Alfred, N.Y.): "Reactions Between Alkaline Earth Sulfates and Cristobalite." J. Am. Ceram. Soc. 46, 125-8 (1963). C.A., 59, 1361 b.

(6) A. Kh. Bronnikov (Chem. Techn. Inst. Ivanovo): "Thermal Stability of Magnesium Sulfate." Izvest. Vysshikh Ucheb. Zavedenii., Khim. i Khim. Tekhnol. 4, 433-6 (1961). C.A., 56, 155 d.

(7) V. V. Pechkovskii, A. G. Zvezdin, and T. I. Beresneva (Polytech. Inst., Perm.): "Kinetics of Thermal Decomposition of Magnesium, Zinc, Copper, and Cobalt Sulfates." Kinetika i Kataliz 4, 208-13 (1963). C.A., 59, 3350 c.

(8) A. Garmute and M. Martynaitis (Polytech. Inst. Kaunas, Lithuania): "The Effect of Oxides on the Thermal Dissociation of Calcium Sulfate." Lietuvos TSR Aukstuju Mokyklu Mokslo Darbai, Chem. ir Chem. Technol. 5, pp. 105-10 (1964). C.A., 61, 5345 f.

(9) M. M. Troyan: "Rate of Thermal Decomposition of Calcium Sulfate." Khim Tekhnol. Miner. Udobr. (Tashkent: Fan) 1966, 279-92 (Russ.). C.A., 66, 108733 c.

(10) N. W. Nathans and W. W. Wendlandt: "The Thermal Decomposition of the Rare-Earth Sulfates, Thermogravimetric and Differential Thermal Analysis Studies up to 1400°C." J. Inorg. and Nucl. Chem. Vol. 24, 1962, pp. 869-879.

(11) Guy Pannetier and André Dereigne: "Thermal Decomposition of Hydrated Lanthanum Sulfate: $La_2(SO_4)_3 \cdot 9H_2O$." Bull. Soc. Chim. France 1963 (8-9), 1850-4. C.A. 60, 1321 d.

(12) A. A. Ivakin (Ural Branch Acad. Sci. U.S.S.R., Sverdlovsk): "Thermal Decomposition of some Rare-Earth Sulfates." Izv. Sibirsk. Otd. Akad. Nauk SSSR 1962, 49-54. C.A., 57, 7964 b.

(13) W. W. Wendlandt: "The Thermal Decomposition of Yttrium and the Rare-Earth Metal Hydrates." J. Inorg. and Nucl. Chem., 7 (1958), pp. 51-54.

(14) Béla Lóránt: "Derivatographische Untersuchung von Sulfaten. Kristallwasserabspaltung und Thermische Zersetung." Z. anal. Chemie, Vol. 219(3), 256-71 (1966).

(15) N. N. Mironov: "Thermogravimetric Studies of Certain Basic Sulfates of Aluminum, Gallium, Iron, Copper and Zirconium." Tr. po Khim. i Khim. Tekhnol. 1964(1), pp. 28-31, C.A. 61 14158 a.

(16) D. Dollimore and K. H. Tonge (Roy. Coll. Advanced Technol., Sulford, Engl.): "Thermal Decomposition of Manganese Oxysalts and the Characterisation of the Solid Products." Intern. Symp. Reactivity Solids 5th, Munich 1964; 497-507, discussion 507-8, (Pub. 1965) (Eng.). C.A., 65, 14824 b.

(17) V. V. Pechkovskii, S. A. Amirova, and N. I. Vorob'ev (Polytech. Inst., Perm.): "Calcination of Green Vitriol (Ferrous Sulfate Heptahydrate) in a Fluidized Bed (Pilot-plant Experiments)." Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6(2), 268-73 (1963). C.A., 59, 9614 g.

(18) Jaromir Trojan and Jiri Nemecek: "Thermal Decomposition of Ferrous Sulfate Heptahydrate in a Fluid Bed Furnace." Czech. 115, 167 (Cl. C 01g), June 15, 1965, Appl. June 11, 1962, 5 pp., C.A., 60, 10199 c.

(19) V. V. Pechkovskii and A. N. Ketov: "Use of Thermographic Methods in the Study of Topochemical Reactions." Uch. Zap Perm. Gos. Univ. 17, No. 1, 15-34 (1960), C.A., 57, 4287 c.

(20) Guy Pannetier, Jean Marie Bregeault, and Gerald Djega-Mariadassou (Fac. Sci., Paris): "Thermal Dissociation of Ferrous Sulfate Heptahydrate." Compt. Rend. 258(10), 2832-5 (1964), C.A., 60, 15419 e.

(21) T. R. Ingraham: "Thermochemistry of the Co-S-O-System from 950 to 1200° K." Canadian Metallurgical Quarterly, Vol. 3, No. 3, July-Sept. 1964, pp. 221-234.

(22) E. V. Margulis and Yu. S. Remizov: "The Chemistry of Thermal Dissociation of Copper, Zinc, Cadmium and Lead Sulfates." Sbornik Nauch. Trudov. Vsesoyuz. Nauch.-Issledovatel Gornomet. Inst. Tsvetn. Met. 1960 No. 6, 171-82. C.A., 56, 3109 a.

(23) V. V. Pechkovskii and M. S. Gaisinovich: "Infrared Spectra of Products of the Thermal Decomposition of Cu, Zn, Cd, and Al-Sulfates." Zh. Neorgan. Khim. 9 (10), 2299-302 (1964) C.A., 62, 1205 a.

(24) T. R. Ingraham, H. H. Kellogg: "Thermodynamic Properties of Zinc Sulfate, Zinc Basic Sulfate, and the System Zn-S-O." Trans. AIME 227, pp. 1419-26, (1963).

(25) Guy Pannetier, Jean Marie Bregeault et Jean Guenot: "Étude de la dissociation thermique des sulfates et des sulfates basiques intermédiaires. I.-Pyrolyse du sulfate de cadmium. Le sulfate basique $CdSO_4 \cdot 2CdO$." Bull. Soc. Chim. France 1962, pp. 2158-63. C.A., 58, 7600 g.

(26) "Treatment of Solid Materials at High Temperatures." North American Coal Corp. (by Ezekail L. Clark). Belg. 638, 611, Feb. 3, 1964; U.S. Appl. Oct. 16, 1962; 23 pp.

(27) H. H. Kellogg and S. K. Basu: "Thermodynamic Properties of the System Pb-S-O to 1100° K." Trans. AIME Vol. 218 (1960) pp. 70-81.

(28) E. V. Margulis, N. S. Grishankina, and N. I. Kopylov: "Thermal Decomposition of Bismuth Sulfate." Russian Journal of Inorganic Chemistry, Vol. 10, Oct., 1965, pp. 1253-1256.

(29) "Proceedings of the First Toronto Symposium on Thermal Analysis." Edited by H. G. McAdie, Toronto Section, Chemical Institute of Canada, February 8, 1965.

(30) T. R. Ingraham: "Making Decomposition Rate Measurements on Simple Inorganic Chemical Powders by T.G.A." Ref. [29], pp. 81-99.

(31) Ref. [30], p. 90, Table III.

(32) S. N. Flengas and T. R. Ingraham: "Equilibrium Decomposition Pressures of K_2TiCl_6." Can. J. Chem. Vol. 38 (1960), pp. 813-817.

(33) R. Spence: "An Accurate Direct Reading Manometer for Corrosive and Other Gases." Trans. Faraday Soc. 36, 417-419 (1940).

(34) A. N. Warner, T. R. Ingraham: "Decomposition Pressures of Ferric Sulfate and Aluminum Sulfate." Can. J. Chem. Vol. 38, (1960), pp. 2196-2202.

(35) K. K. Kelley: "Contributions to the Data on Theoretical Metallurgy." U.S. Department of Interior, Bureau of Mines, Bulletin 383, pp. 1-4.

(36) T. R. Ingraham: "Thermodynamics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate." Transactions of the Metallurgical Society of AIME Volume 233, Feb., 1965, pp. 359-367.

(37) T. R. Ingraham: "Thermodynamics of the Mn-S-O System between 1000° K and 1250° K." Can. Met. Quart. Vol. 5, 1966, Number 2, pp. 109-122.

(38) T. R. Ingraham: "Proceedings of the First International Meeting on Applications of Fundamental Thermodynamics to Metallurgical Processes." Ed. by G. Fitterer. Gordon and Breach, New York, (1967).

(39) T. R. Ingraham: "Thermochemistry of the Co-S-O System from 950-1200° K." Can. Met. Quart. Vol. 3, No. 3, July-Sept. 1964, pp. 220-234.

(40) T. R. Ingraham: "Thermodynamics of the Thermal Decomposition of Nickel (II)-Sulfate: The Ni-S-O System from 1000° K to 1150° K." Trans. Met. Soc. AIME 236(7), 1966, pp. 1064-7.

(41) H. H. Kellogg: "A Critical Review of Sulfatation Equilibria." Trans, AIME 230, (1964), pp. 1622-34.

(42) Guy Pannetier, Jean Marie Bregeault, Gerald Djega-Mariadassou et Monique Grandon: "Etude de la dissociation thermique des sulfates et des sulfates basiques. IV.-Cas des hydroy-sulfates de cuivre $CuSO_4$, $2Cu(OH)_2$ et $CuSO_4$, $3Cu(OH)_2$, xH_2O." Bull. Soc. Chim. France 1963 (11), pp. 2316-19.

(43) V. V. Pechkovskii and M. S. Gaisinovich: "Infrared Spectra of Products of the Thermal Decomposition of Copper, Zinc, Cadmium and Aluminumsulfates." Russian Journal of Inorganic Chemistry, October, 1964, Vol. 9, No. 10, pp. 1245-47.

(44) B. E. Warren and B. L. Averbach: "The Effect of Cold-Work Distortion on X-Ray Patterns." Journal of Applied Physics 23 (1952), p. 497. Ibid 21 (1950), pp. 595-599.

(45) V. V. Pechkovskii: "Mechanism of Oxidizing Roasting of Sulfide Ores." Nauch. Trudy, Novocherkassk. Politekh. Inst. im. S. Ordzhonikidze 26, pp. 268-75 (1955), C.A., 51, 12782 d.

(46) Wienczyslaw Kuczynski and Wlodzimierz Kania: "Oxidation of Sulfur Dioxide on Nonmodified Chromia-Alumina Catalysts." Przem. Chem. 45 (12), pp. 659-62, (1966) (Pol). C.A., 66, 08674 z.

(47) M. B. Kartsynel and A. I. Chernikov: "Adsorption of Sulfur Dioxide in the presence of a Chromium-Tin Catalyst." Trudy Dnepropetrovsk. Khim.-Tekhnol. Inst. 1958, No. 6, 66-71. C.A., 55, 6098 h.

(48) Tetsuro Seiyama, Akio Suenaga, and Wataru Sakai: "Thermodynamic Consideration on Catalytic Oxidation of Carbon Monoxide and Sulfur Dioxide." Nippon Kagaku Zasshi 82, pp. 292-8, (1961). C.A., 55, 19422 d.

(49) Georg Maria Schwab und Emmanuel Kaldis: "Zum elektronischen Mechanismus der katalytischen SO_3-Bildung an Cr_2O_3-Kantakten." Zeitschrift fur Physikalische Chemie Neue Folge, Bd. 42, pp. 72-81 (1964).

(50) Giuseppe Greco: "Catalytic Oxidation of Sulfur Dioxide to Sulfur Trioxide." Brit. 749, 645, May 30, 1956: C.A. 50 P 16059 b.

(51) Earl V. Harlow: (to Koppers Co., Inc.) "Conditioning of Stack Gases for Electrostatic Precipitators." U.S. 2, 746, 563, May 22, 1956. C.A. 50 P 12449 f.

(52) G. H. Tandy: "The Role of Alkali-Sulfates in Vanadium Catalysts for Sulfur Dioxide Oxidation." J. Appl. Chem. (London) 6, pp. 68-74, (1956). C.A., 51, 17637 a.

(53) V. V. Illarionov: "Phase Condition of Active Component in Vanadium Catalysts of Sulfur Dioxide Oxidation." Geterogennyĭ Kataliz v Khim. Preom. (Moscow; Gosudarst. Nauch. Tekh. Izdatel. Khim. Lit.) Sbornik 1955, pp. 393-5. C.A., 52, 17637 a.

(54) E. I. Makarova and V. V. Illarionov: "Study of the Active Component in Vanadium Catalysts by the Sulfur Exchange Method." Vanadievye Katalizatory Klya Kontaktn. Proizv. Sernoi Kisloty, Nauchn.-Issled. Inst. Udobr. i Insektofung., Sb. Statei 1963, pp. 68-75. C.A., 60, 8683 b.

(55) Pavel Jiru and Vladimir Jara: "Effect of Alkali Metal Sulfates on the Activity of Vanadium Pentoxide for the Catalytic Oxidation of Sulfur Dioxide." Actes intern. Congr. catalyse, 2^e, Paris, 1960, 2, pp. 2113-18, discussion p. 2119, (Pub. 1961). C.A., 55, 23009 h.

(56) P. Mars and J. G. H. Maessen: "The Mechanism of the Oxidation of Sulfur Dioxide on Potassium-Vanadium Oxide Catalyst." Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964, 1, pp. 266-79, discussion pp. 278-81, (Pub. 1965). C.A., 63, 12369 d.

(57) Pavel Jiru: "Effect of the Alkali Metal Sulfates on the Activity of Vanadium Pentoxide in the Catalytic Oxidation of Sulfur Oxide." Vanadievye Katalizatory dlya Kontaktn. Proizv. Sernoi Kisloty, Nauchn.-Issled. Inst. Udobr. i Insektofung., Sb. Statei 1963, pp. 21-35. C.A., 23, 69 h.

(58) "Manufacture of an Oxidation Catalyst for Use at High Temperatures." Deutsche Gold-and Silber-Scheideanstalt vorm. Roessler. Fr. 1,467, 334 (Cl. B 01j, A 61ℓ), Jan 27, 1967; Ger. Appl. Feb. 3 and Sept. 24, 1965, 4 pp. C.A., 66, 76123 w.

(59) D. H. Napier and M. H. Stone: "Catalytic Oxidation of Sulfur Dioxide at Low Concentrations." J. Appl. Chem. 8, pp. 781-6, (1958).

(60) E. V. Gerburt, I. M. Gleikhengauz, B. T. Vasil'ev, and V. V. Illarionov: "Search for Catalysts for the Oxidation of Sulfur Dioxide with a Decreased Ignition Temperature." Vanadievye Katalizatory dlya Kontaktn. Proizv. Sernoi Kisloty, Nauchn.-Issled, Inst. Udobr. i Insektofung, Sb. Statei 1963, pp. 36-42, C.A., 60, 3524 b.

(61) G. S. John, M. J. Den Herder, R. J. Mikovsky, and R. F. Waters: "Physicochemical Studies of Molybdena Reforming Catalysts." Advances in Catalysis 9, pp. 252-67, (1957), C.A., 53, 1692 a.

(62) A. S. Kuznoetsova, L. M. Skrebkova, and B. S. Khristoforov: "Phase Analysis of Iron-Molybdenum Catalysts." Kinetika i Kataliz 7(2), pp. 354-5 (1966)(Russ.). C.A., 65, 3051 e.

(63) N. Flood and O. J. KLeppa: "Investigations on the Equilibria in the System V_2O_4, V_2O_5, $VOSO_4$, SO_2, SO_3." J. Am. Chem. Soc. 1947, Vol. 69, pp. 998-1002.

(64) A. M. Ginstling and M. D. Volkov: "Reactions of Elemental Sulfur Formation in the Interaction of (Calcium Sulfate with Carbon." Zhurnal Prikladnoi Khimii, Vol. 33, No. 8, pp. 1700-1704 (1960).

(65) V. V. Pechkovskii and T. Y. Mal'tseva: "The Interaction between Calcium Oxide and Sulfur Dioxide under Reducing Conditions." Zhurnal Prikladnoi Khimii, Vol. 37, No. 2, pp. 240-246, Feb., 1964.

(66) V. V. Pechkovskii and A. N. Ketov: "Study of the Reduction of Barium Sulfate by Carbon Monoxide at High Temperatures." Zhurnal Prikladnoi Khimii Vol. 33, No. 8, pp. 1719-1723, August, 1960.

(67) V. V. Pechkovskii: "Rules for the Formation of Sulfides and Oxides of Metals in the Thermochemical Decomposition of the Sulfates of Manganese and Iron." Journal of Applied Chemistry of the USSR Vol. 32, (1959), pp. 2691-2696.

Copy made for Chemistry Files

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

6 May 1968 K. Schwitzgebel

TECHNICAL MEMORANDUM 004-009-Ch 3
THERMAL DECOMPOSITION OF SOME METAL SULFITES

C. Castellani and coworkers (1) investigated quantitatively the thermal decomposition of Li-, K-, Sr-, Ba-, Pb-, Ag-, Tl-, La-, Sm-, Y-, Zn-, Cd-, Mn-, Hg-, and Mg-sulfites.

The experiments were performed in the following manner: The sulfites were heated at a rate of 10° C/Min. They were held for one hour at the final temperature, next they were cooled and analyzed. The samples were in a glass tube with a stream of nitrogen passing over them throughout the experiment.

Some experiments have been performed in an autoclave. For $PbSO_3$ it was observed that the disproportionation reaction was more dominant in the autoclave experiments than in the experiments using a nitrogen stream.

The sulfites under investigation can be divided into three groups. Group 1: Sulfites, which disproportionate almost entirely to form sulfates and sulfides. The alkali-metal-sulfites belong to this group. Figure 1 shows the results obtained with lithium-sulfite. (residuo = unreacted; dissociato = decomposed; dismutato = disproportionated)

Only 1-2% of the starting material decomposed to $Li_2O + SO_2$:

$$Li_2SO_3 \rightarrow Li_2O + SO_2$$

Group 2: The metal sulfites belonging to this group (Ca, Sr, Ba, Zn, La, Sm, Cd, Pb, Mn, Tl) show both: Disproportionation and decomposition. Figure 2 shows the results obtained with $PbSO_3$ in

FIGURE I

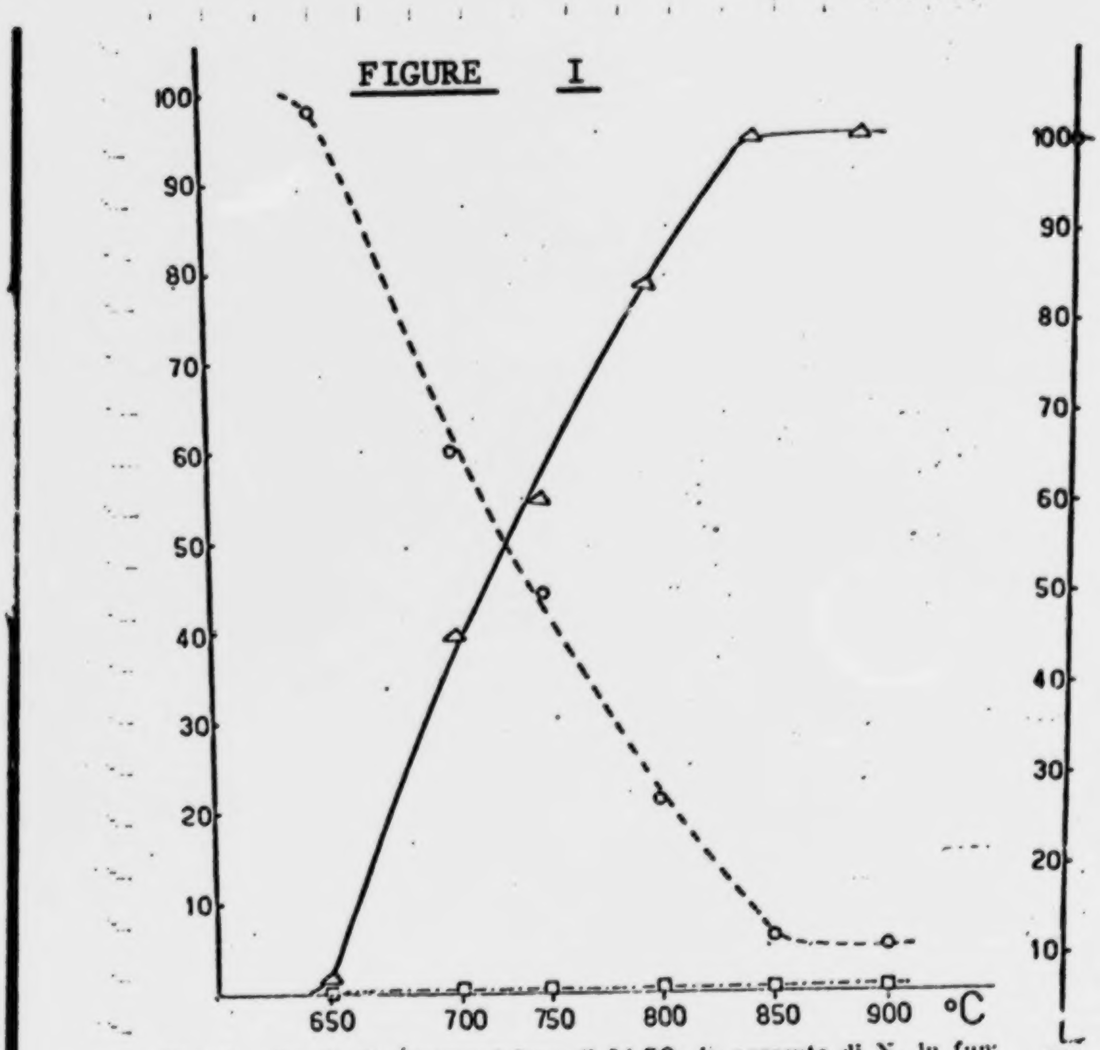


Fig. 2. - Grado di decomposizione di Li_2SO_3 in corrente di N_2 in funz. della temperatura

— — — Li_2SO_3 residuo (unreacted)
---.--- Li_2SO_3 dissociato decomposed
——— Li_2SO_3 dismutato disproportionated

Fig. 1.

C. Castellani Bisi, E. Res Garrini, "Thermal Decomposition of Some Metal Sulfites," Gazz. Chim. Ital., vol. 93, no. 10, pp. 1252-8 (1963).

a N_2-stream and in the autoclave. In the experiment under nitrogen a greater amount of the starting material decomposed. But as the graph show, a large part of the starting material still disproportionated:

$$4\ PbSO_3 \rightarrow 3\ PbSO_4 + PbS$$

FIGURE II

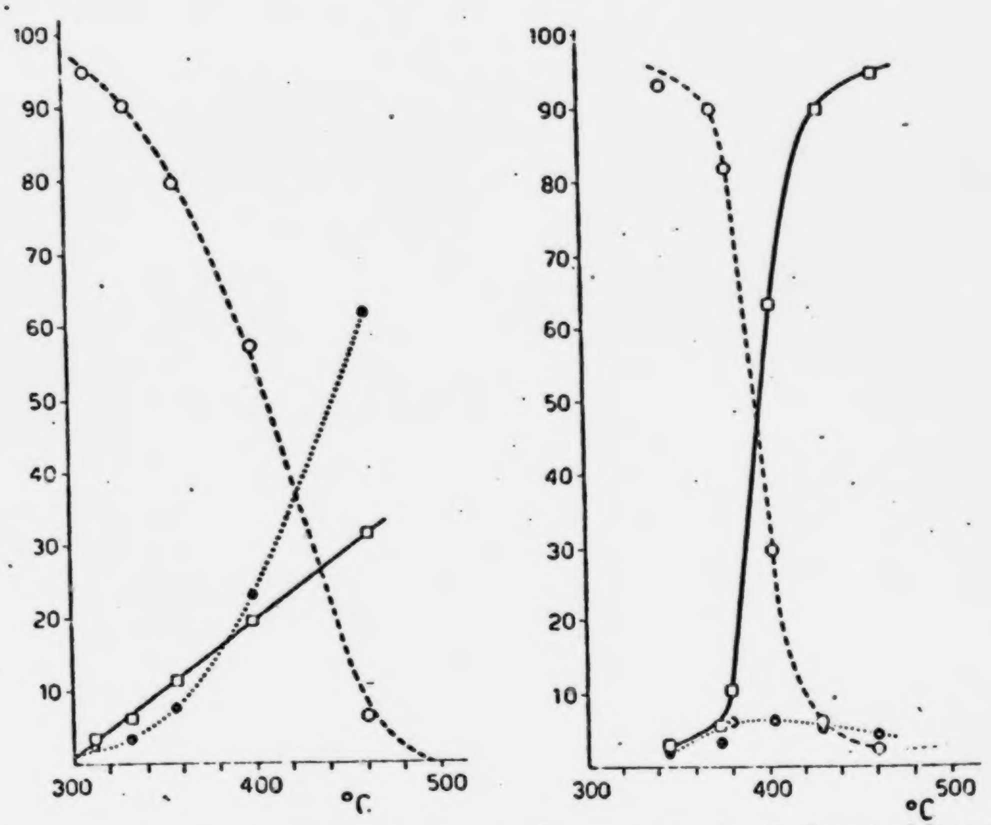


Fig. 5. - Grado di decomposizione di $PbSO_3$ in corrente di azoto in funzione della temperatura

- - - - - $PbSO_3$ residuo
—·—— $PbSO_3$ dismutato
.... $PbSO_3$ dissociato

Fig. 6. - Grado di decomposizione di $PbSO_3$ in autoclave in funzione della temperatura

- - - - - $PbSO_3$ residuo
——— $PbSO_3$ dismutato
.... $PbSO_3$ dissociato

M. Cola, C. Castellani Bisi, "Thermal Decomposition of Some Metal Sulfites," Gazz. Chim. Ital., vol. 91, pp. 173-86 (1961).

Group 3: The metal-sulfites of this group show minimal characteristics due to secondary reactions. Hg and Ag decompose forming sulfate and metal. Mg forms thiosulfate.

In the experiments with samarium and lanthanum the following reaction was observed due to the presence of water of crystallization.

$$La_2S_3 + 3H_2O \rightarrow La_2O_3 + H_2S$$

Castellani proposed for the disproportionation reaction the following mechanism:

$4\ Me_2SO_3 \rightarrow 2\ Me_2SO_4 + 2\ Me_2SO_2$ Me = univalent

$2\ Me_2SO_2 \rightarrow Me_2S_2O_3 + Me_2O$

$Me_2O + Me_2S_2O_3 \rightarrow Me_2SO_4 + Me_2S$

$4\ Me_2SO_3 \rightarrow 3\ Me_2SO_4 + Me_2S$

or

$4\ MeSO_3 \rightarrow 3\ MeSO_4 + MeS$ for a bivalent metal

The SO_2 from the decomposition reaction

$$MeSO_3 \rightarrow MeO + SO_2$$

can react with the sulfite as follows:

$$2\ SO_2 + 3\ Me_2SO_3 \rightarrow 3\ Me_2SO_4 + S_2O$$

and

$$SO_2 + Me_2SO_3 \rightarrow Me_2SO_4 + SO$$

Thermodynamic Consideration

The reaction path found by Castellani and coworkers indicates that at higher temperatures the sulfites are unstable. Whether the disproportionation or the decomposition reaction occurs depends upon the thermodynamic equilibrium and the reaction kinetics.

The phase rule indicates that the reaction

$$4\ MeSO_3 \rightleftharpoons 3\ MeSO_4 + MeS$$

will go to 100% completion in the direction thermodynamically favored. This is due to the fact that in a three component system with three solid phases there exists only one degree of freedom. For a given pressure, there exists only one temperature at which all three phases can be present. This temperature is given by the relation:

$$\Delta G = \Delta H - T\Delta S = 0$$

or

$$T = \frac{\Delta H}{\Delta S} \approx \frac{\Delta H^\circ}{\Delta S^\circ}$$

For temperatures where ΔG is negative, disproportionation occurs. For temperatures where ΔG is positive, the sulfite is stable. The sulfite decomposes when the partial pressure of SO_2 is smaller than the equilibrium pressure.

$$MeSO_3 \rightleftharpoons MeO + SO_2$$

In order to investigate these thermodynamic areas of stability for the sulfites, the sulfides have to be included into the literature search.

Preliminary calculations indicate that at 298° K, aluminum and beryllium sulfite are stable. No literature was found discussing the stability beryllium sulfite. The behaviour of aluminum sulfite was investigated by Dybina (2,3). Dybina reports a complete decomposition at 450-550° C for the crystallized sulfites, and at 600° C for amorph~~es~~ous sulfites. In Chemical Abstracts there is nothing mentioned about a disproportionation. This agrees with the thermodynamic calculation. The original articles are ordered, but they have not arrived.

For the behaviour of $ZnSO_3$, the articles found in the literature are contradictory. Pechkovskii and Ketov (4) report that above 350° C the products of decomposition contained ZnS and $ZnSO_4$. In a French article (5) the formation of 2 $ZnSO_4 \cdot ZnO$ at temperatures >320° C is reported. Tibor Bakay (6) reports that at 400-500° C $ZnSO_3$ can be decomposed forming ZnO and SO_2.

LITERATURE

1. Carla Castellani and coworkers:
   Gazz. Chim. Ital. 93, (10), 1252-8 (1963)
   92, 447-53 (1962)
   93, (11), 1444-54 (1963)
   91, 173-86, (1961)
2. P. V. Dybina, "Thermal Stability of Aluminum Sulfites", Izvest. Vysshikh. Ucheb. Zavedeniĭ, Khim. i Khim. Tekhnol. 3, 902-7 (1960).
3. P. V. Dybina, "X-ray Examination of Aluminum Sulfites", Sb. Statei Vses. Zaochn. Politekhn. Inst. No. 32, 10-14 (1964).
4. V. V. Pechkovskii and A. N. Ketov, "Thermal Decomposition of Zinc Sulfite", Zhur. Priklad. Khim. 33, 1724-9 (1960).
5. Guy Pannetier, "Decomposition Occurring with Simultaneous Release of Several Gases", Bull. Soc. Chim. France 8, 1749-56 (1964).
6. Tibor Bakay, "Decomposition of $ZnSO_3$ Obtained from the Purification of Fume Gas Which Contains Sulfur Dioxide", Metallgesellschaft A.-G., Fr. 1,370,320 (Cl.C01b), Aug. 21,1964.

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

TECHNICAL MEMORANDUM 004-009-Ch16

INTERACTION OF SULFUR DIOXIDE WITH DRY METAL OXIDES

and

SELECTION OF OXIDES AS POTENTIAL SORBENTS

31 December 1968

Prepared by:

Klaus Schwitzgebel
Klaus Schwitzgebel

Terry B. Parsons
Terry B. Parsons

TABLE OF CONTENTS

I. INTRODUCTION. 1

II. PHYSICAL AND CHEMICAL PROPERTIES OF SULFITES. 3

  A. Sorption of SO_2 on metal oxides with formation of sulfite. 3

  B. Disproportionation and decomposition of sulfites. 42

III. ADSORPTION ON ACTIVE OXIDES WITH SULFATE FORMATION. . 104

IV. CATALYTIC OXIDATION OF SO_2. 116

V. CORRELATION OF DATA - SELECTION OF POTENTIAL SORBENTS. 147

VI. REFERENCES. 157

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

T.M. 004-009-Ch16
31 December 1968

I. INTRODUCTION

The purpose of this memorandum is to collect all thermodynamic information available concerning the interaction of dry metal oxides and sulfur dioxide.

The first thing we have considered is the possibility of SO_2 sorption with resulting formation of sulfites and the subsequent decomposition of the sulfites. Most of the information given here is based on thermodynamic calculations using data from the TRACOR data base. Most of the thermodynamic data for the sulfites were estimated.

It was found from the experimental results reported in the literature that most sulfites tend to disproportionate to sulfate and sulfide. This tendency was predicted from thermodynamic calculations and compared with the reported experimental results. Only the sulfites of beryllium, thorium, uranium, and aluminum were found to have no disproportionation tendency. Experimental support for these predictions was not found in the literature. From the reported experimental results, we have found the following to be generally true. When a sulfite has a high decomposition temperature, the disproportionation reaction occurs to a large extent. For sulfites with lower decomposition temperatures, disproportionation and decomposition are competing reactions.

The economic advantages of thermal regeneration exclude the possibility of applicability of the alkali metal and most of the alkaline earth oxides. The transition metal oxides are therefore of importance. Since it is known that most of the transition metal oxides show catalytic activity for SO_2 oxidation, two necessary steps were indicated. First, it was necessary to describe the principles that govern catalytic activity, second, the literature was surveyed in an attempt to describe the behavior of catalytically effective oxides in SO_2 oxidation.

It was found that catalytic effectiveness of an oxide and sorption on an oxide with the formation of sulfate are closely related. The main difference is the partial pressure of SO_3 over the sulfate intermediate.

Finally, all available data have been correlated in Table 37. Table 37 is a succinct survey of the more detailed information given in Parts II, III, and IV, T.M. 004-009-Ch6, and T.M. 004-009-Ch8.

The selection of oxides as potential sorbents as presented in Part V was based mainly on thermodynamic considerations with the viewpoint that the sorbent should be thermally regenerable at temperatures less than 800 to 900° C. It is important to note that the collection of kinetic data must be the next step for further screening.

II. PHYSICAL AND CHEMICAL PROPERTIES OF SULFITES

A. Sorption of SO_2 on Metal Oxides with Formation of Sulfite

Partial pressure measurements of SO_2 over sulfites as a function of temperature could not be found in the literature. This is probably due to the fact that at high temperatures many of the sulfites are metastable at best and tend to disproportionate.

Thermodynamic quantities are also very scarce. In order to calculate the partial pressures as well as possible disproportionation reactions, most of the heats of formation, standard entropies, and heat capacities as a function of temperature had to be estimated. The methods of estimation are described in Technical Memoranda 004-009-Ch1, 004-009-Ch1A, 004-009-Ch2, 004-009-Ch4, 004-009-Ch5, and 004-009-Ch13.

In order to describe the possibilities for sorption of SO_2 by metal oxides with the reaction product being the metal sulfite, the partial pressures of SO_2 were calculated as a function of temperature for the following reaction:

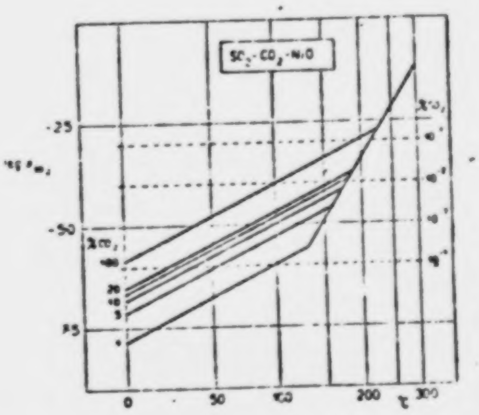
$$Me_XSO_3 \rightleftharpoons SO_2 + Me_XO \qquad (1)$$

Sorption of SO_2 under flue gas conditions, down to a lower concentration limit of $[SO_2] = 150$ ppm, is theoretically possible for the temperature range in which $\log Kp \leq -4$.

In this section we consider only the theoretical reactions for which the products are anhydrous sulfites. In actuality, hydrated sulfites, as well as basic sulfites, may be the reaction products at lower temperatures. It is not known, however, which metal oxides form basic sulfites. Therefore, the temperature range predicted for sorption is only an approximation. The decomposition temperature is considered to be close to the experimentally determined value (see case of $ZnSO_3 \cdot \frac{5}{3} H_2O$), since the water of crystallization is given off at temperatures far below the decomposition temperature.

From phase rule considerations, it is known that an increase in the CO_2 concentration in the gas phase increases the fugacity of the SO_2 required for reaction at temperatures below that of the carbonate decomposition. The flue gas is composed of about 15% CO_2. If the carbonate has not decomposed at the maximum predicted sorption temperature, the temperature prediction based on oxide only may be too high. More rigorous calculations would take these facts into consideration. An example of the effect of the presence of CO_2 is shown in Figure 1 for the case of the SO_2-CO_2-NiO equilibrium (ER-003).

FIGURE 1: EQUILIBRIUM IN THE SYSTEM SO_2-CO_2-NiO



r) SO_2-CO_2-NiO

E. ERDOS, 'EQUILIBRIA IN THE SYSTEMS SO2-CO2-MO,' COLL. CZECH. CHEM. COMMUN., VOL. 27, P. 2152-67 (1962).

Secondary reactions such as disproportionation of the sulfite or catalytic activity of the oxides are not considered in this section. These aspects will be covered in later sections of this report. In Table 37, all of the available information about the behavior of each metal oxide is assembled.

The equilibrium constant for the decomposition of a sulfite to form SO_2 and a metal oxide (Equation 1) is numerically equal to the partial pressure of SO_2 in atmospheres. Hence, the decomposition reaction has been calculated to show the effect of temperature on SO_2 sorption capability. No side reactions have been considered.

Results:

1) $$Li_2SO_3 \rightarrow SO_2 + Li_2O \qquad (2)$$

Sorption: Possible up to > 800° C
Thermal Regeneration: Not possible between 25 and 800° C
(See Figure 2)

2) $$Na_2SO_3 \rightarrow SO_2 + Na_2O \qquad (3)$$

Sorption: Possible up to > 800° C
Thermal Regeneration: Not possible between 25 and 800° C
(See Figure 3)

3) $$K_2SO_3 \rightarrow SO_2 + K_2O \qquad (4)$$

Sorption: Possible up to > 800° C
Thermal Regeneration: Not possible between 25 and 800° C
(See Figure 4)

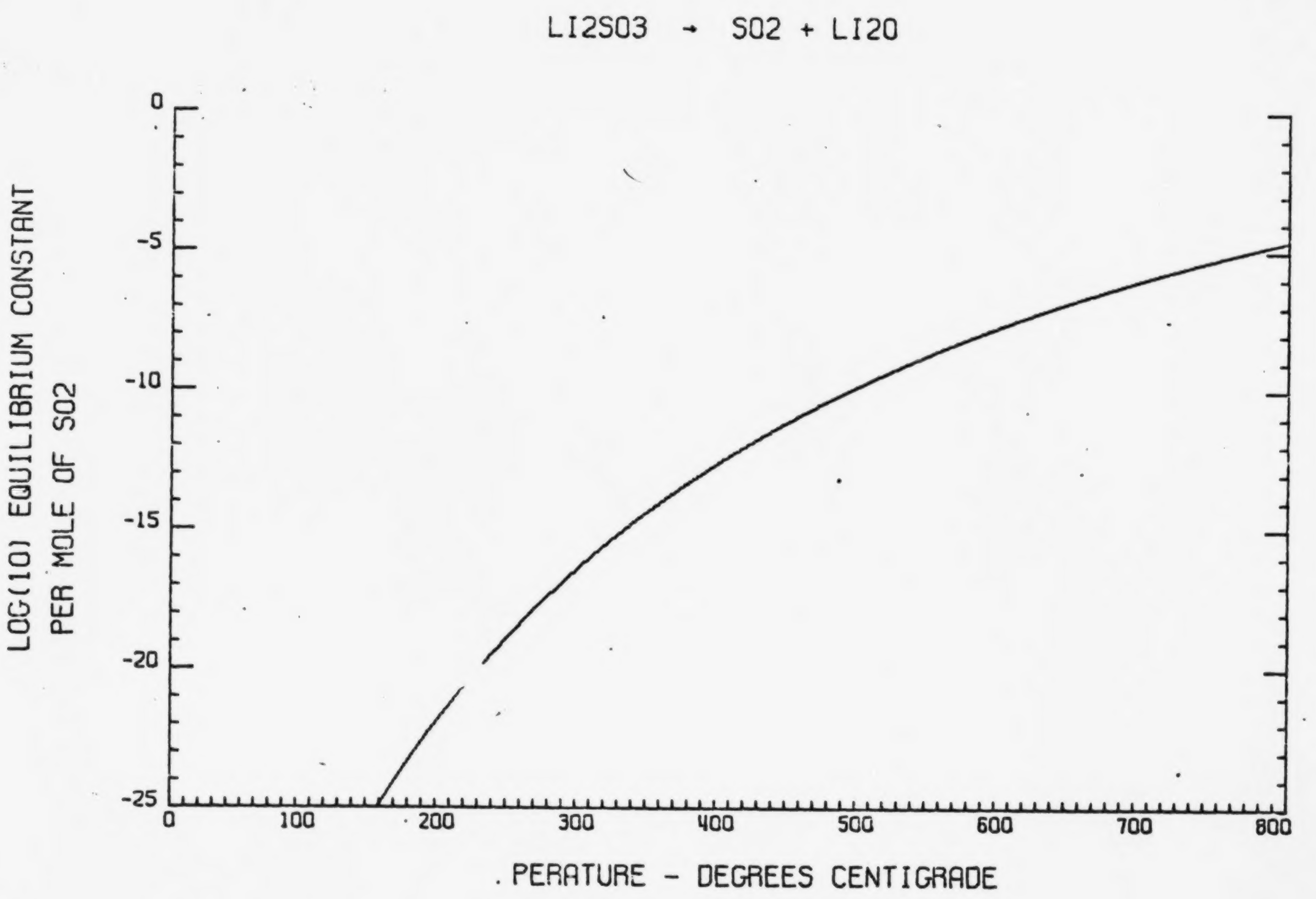

LI2SO3 → SO2 + LI2O
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
PERATURE - DEGREES CENTIGRADE

FIGURE 2

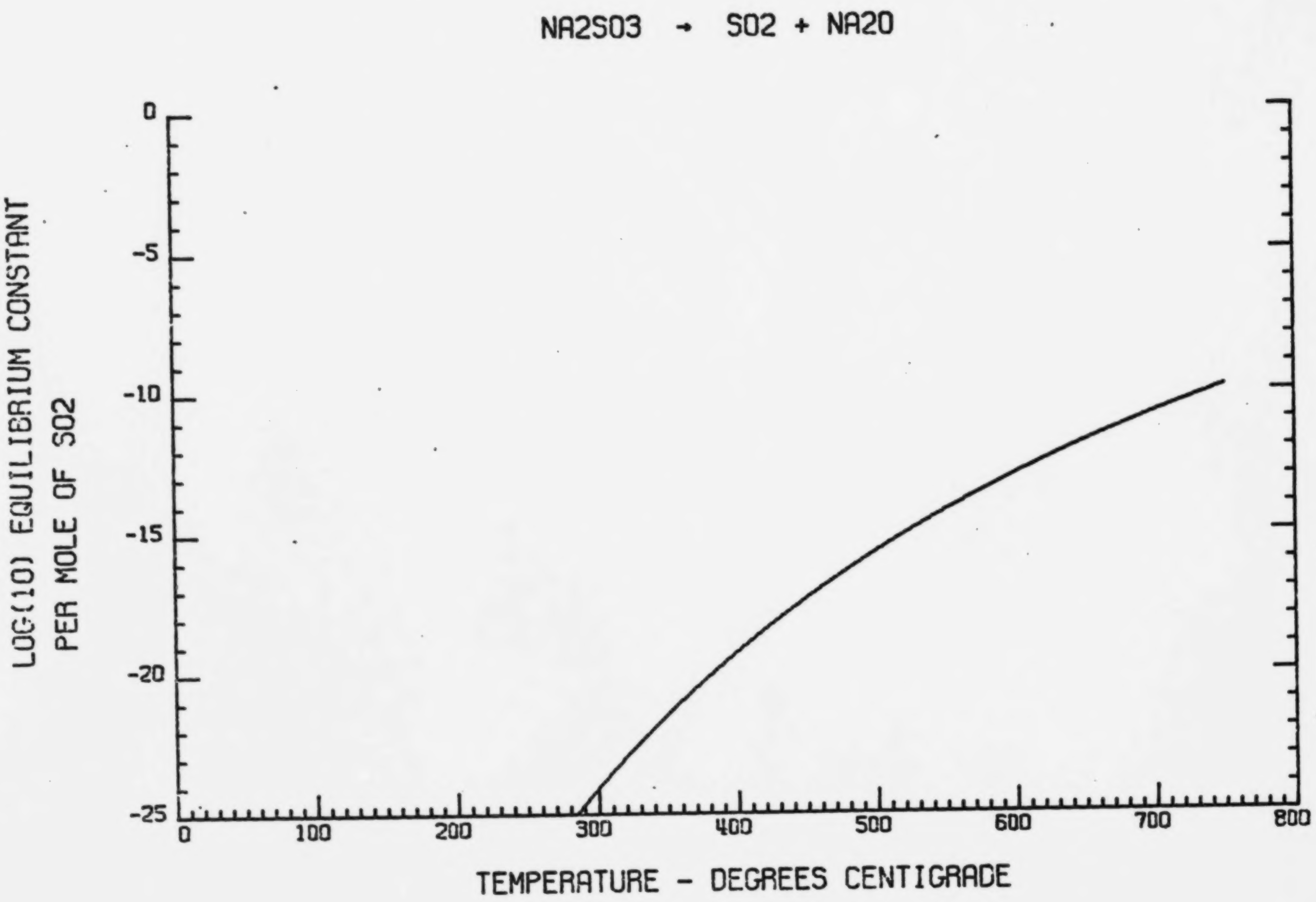

NA2SO3 → SO2 + NA2O

FIGURE 3

27 JUN 68

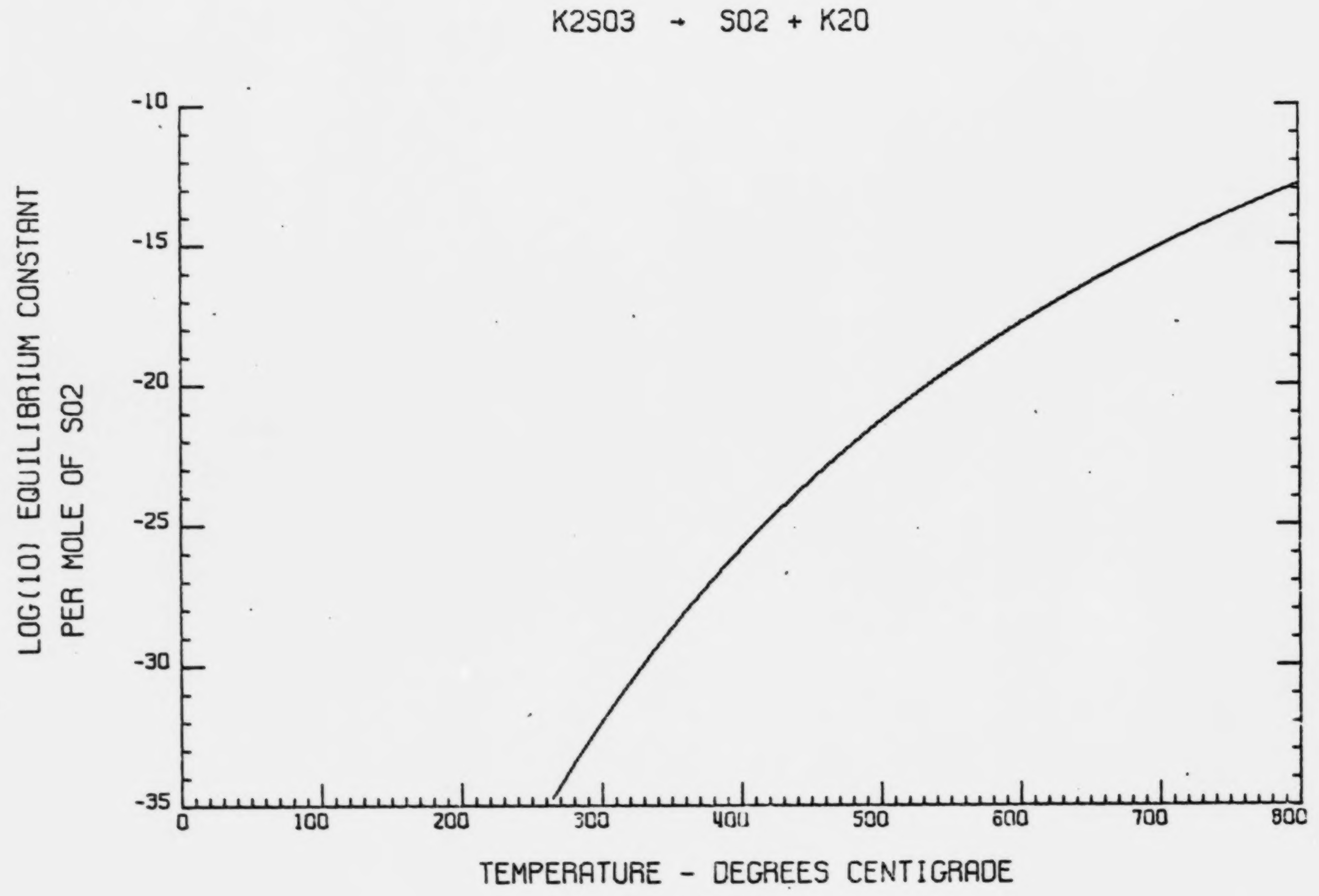

K2SO3 → SO2 + K2O
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
-10
-15
-20
-25
-30
-35
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 4

4) Rb_2SO_3 and Cs_2SO_3

No estimation is possible. There is a lack of heat capacity data. The results for Li, Na, and K, however, indicate that the stability of the sulfites increases with increasing atomic numbers. Based on this fact, one can predict that sorption will be possible in the entire temperature range. However, there will be no chance of thermal regeneration.

5) $BeSO_3 \rightarrow BeO + SO_2$ (5)

Sorption: Not possible above 25° C
(See Figure 5)

6) $MgSO_3 \rightarrow SO_2 + MgO$ (6)

Sorption: Possible at temperatures < 150° C
Thermal Regeneration: Possible at temperatures > 350° C
(See Figure 6)

7) $CaSO_3 \rightarrow SO_2 + CaO$ (7)

Sorption: Possible at temperatures < 590° C
Thermal Regeneration: Not possible below 800° C
(See Figure 7)

8) $SrSO_3 \rightarrow SO_2 + SrO$ (8)

Sorption: Possible in the range from 25 to 800° C
Thermal Regeneration: Not possible below 800° C
(See Figure 8)

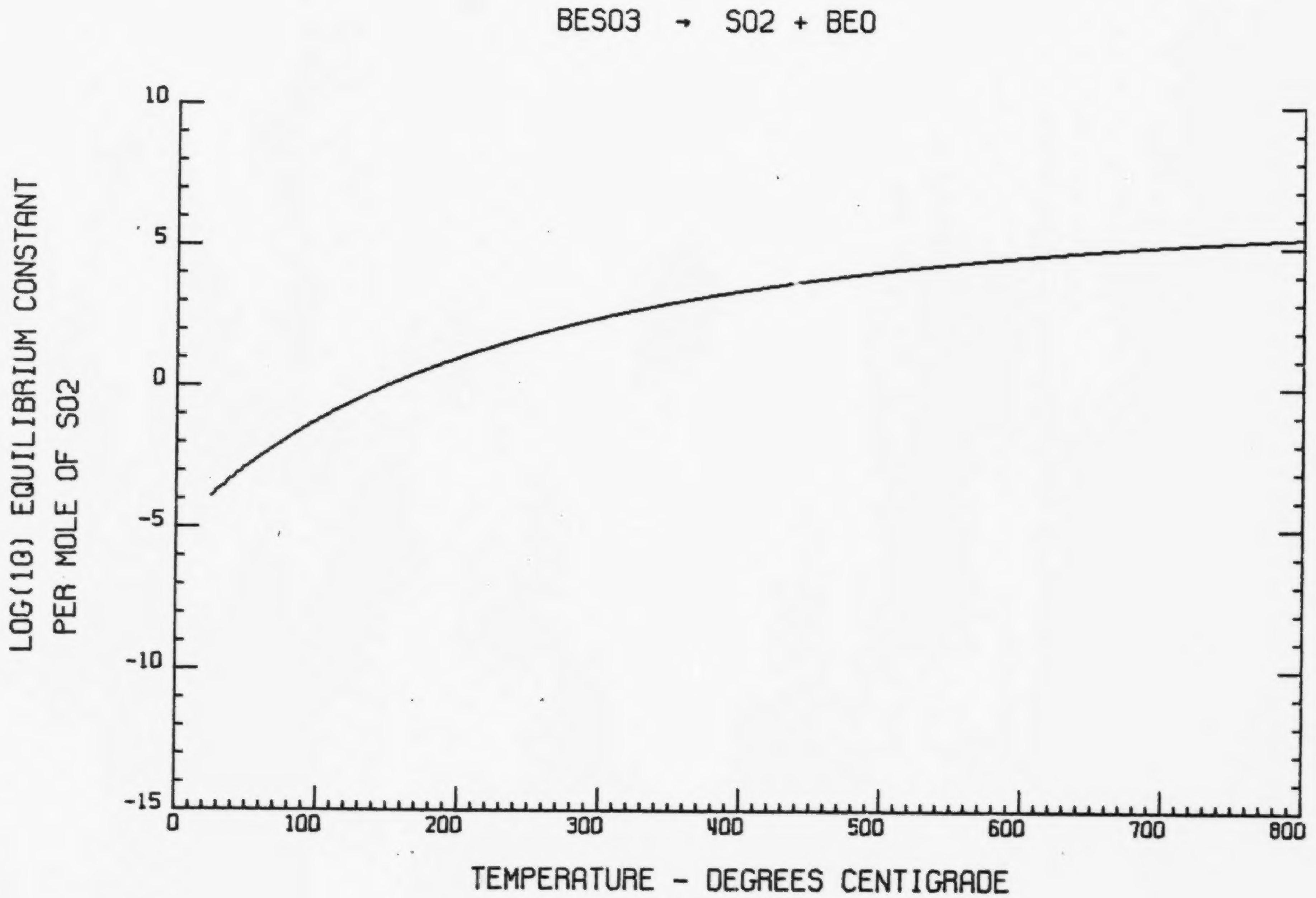


FIGURE 5

12 DEC 68

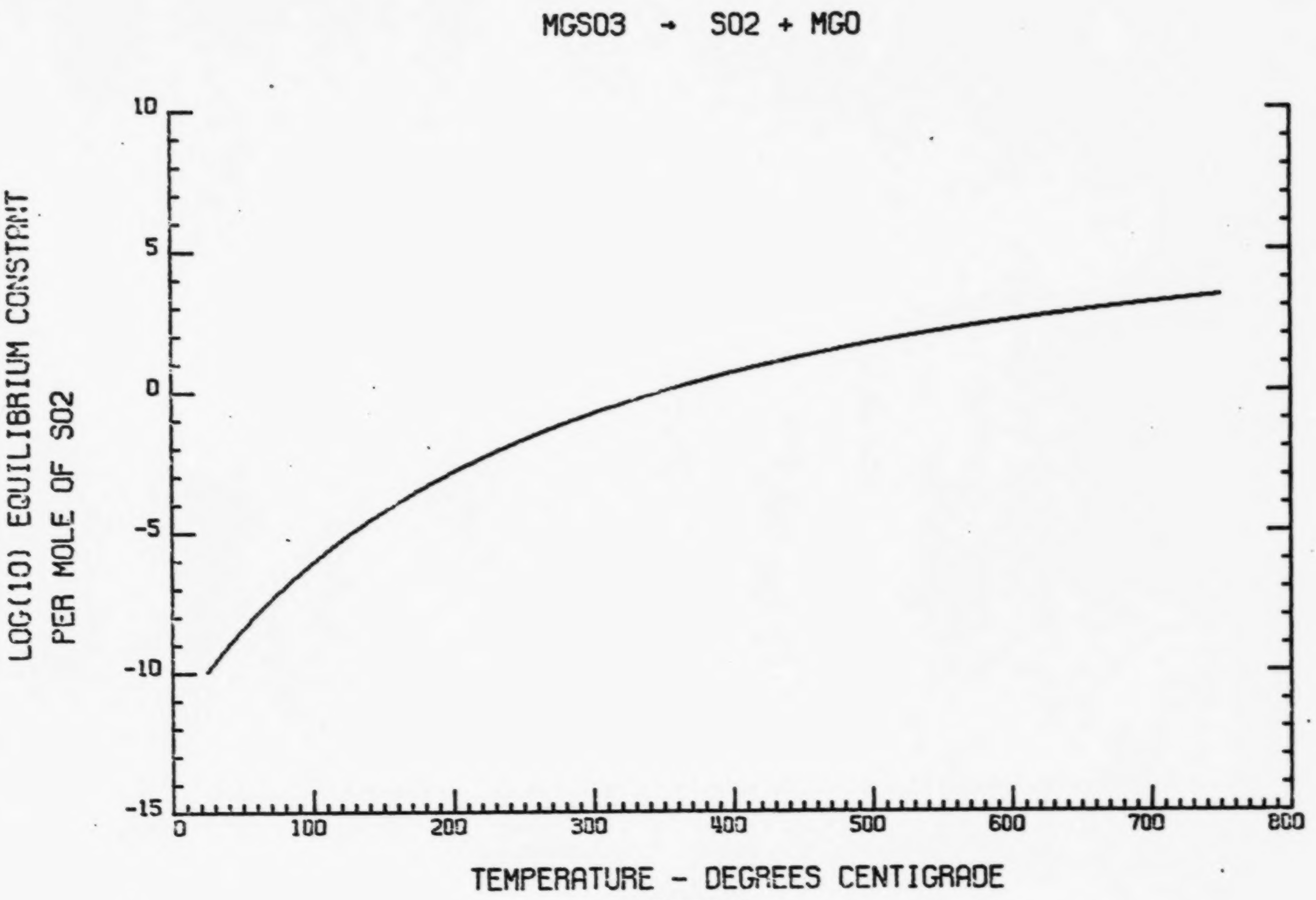

MGSO3 → SO2 + MGO
LOG(10) EQUILIBRIUM CONSTANT PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 6

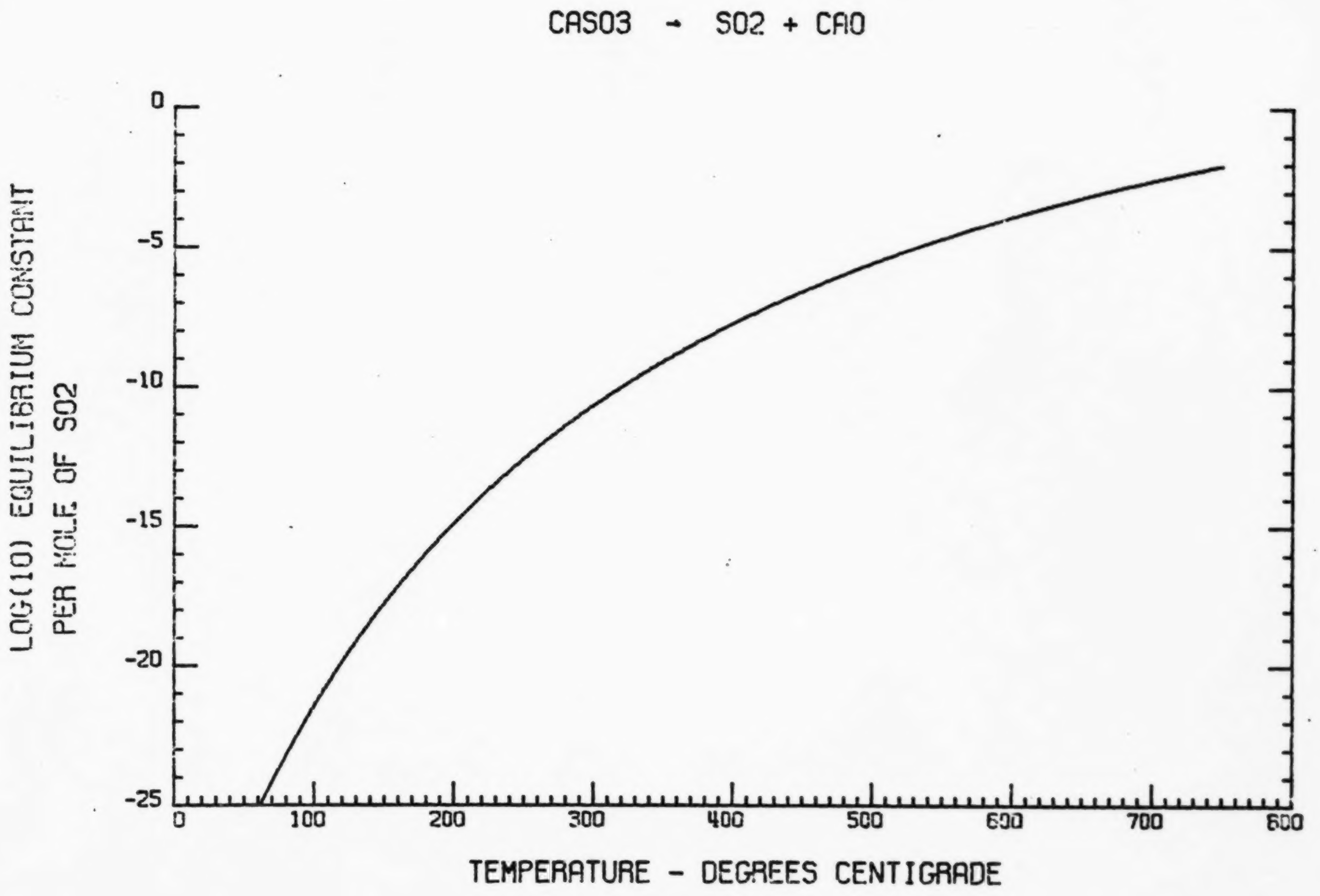

CASO3 → SO2 + CAO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 7

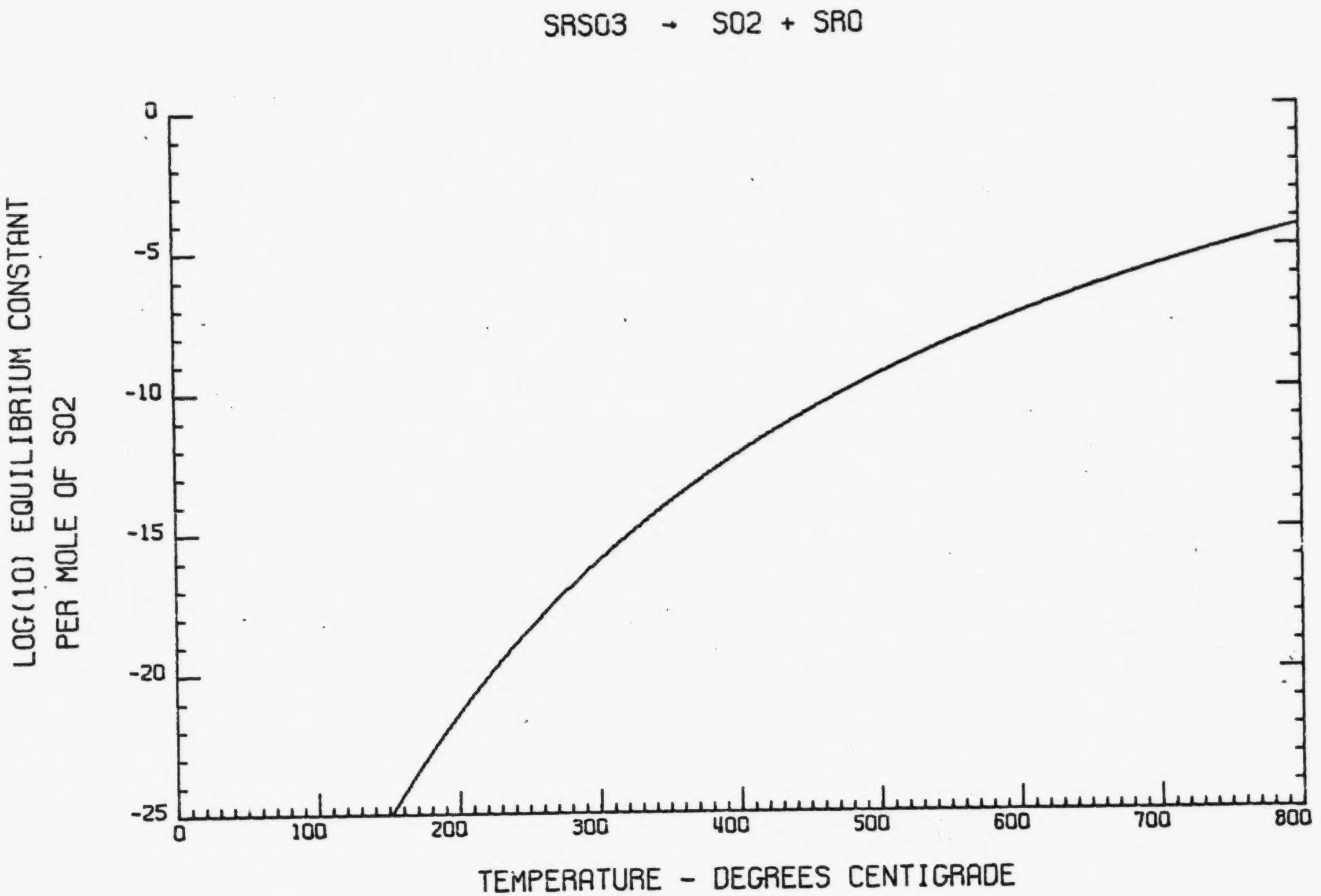

SRSO3 → SO2 + SRO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 8

9) $BaSO_3 \rightarrow SO_2 + BaO$ (9)

Sorption: Possible in the range from 25 to 800° C
Thermal Regeneration: Not possible below 800° C
(See Figure 9)

10) Scandium Sulfite
11) Yttrium Sulfite

For the sulfates and carbonates of scandium and yttrium, there are few thermodynamic data for the heat of formation. The estimation of the corresponding values for the sulfites was therefore not attempted.

12) Lanthanum Sulfite

A value for lanthanum sulfite was not estimated. The heats of formation given in the literature for La_2O_3 are conflicting. The value given for the sulfate seems too high (See T.M. 004-009-Ch18).

13) Cerium Sulfite

No estimation was made because the literature values for CeO_2 and Ce_2O_3 conflict. (See Technical Memorandum 004-009-Ch18.)

14) Titanium Sulfite

Heat of formation of the corresponding sulfate is not known. Therefore, an estimation of the heat of formation for the sulfite was not made.

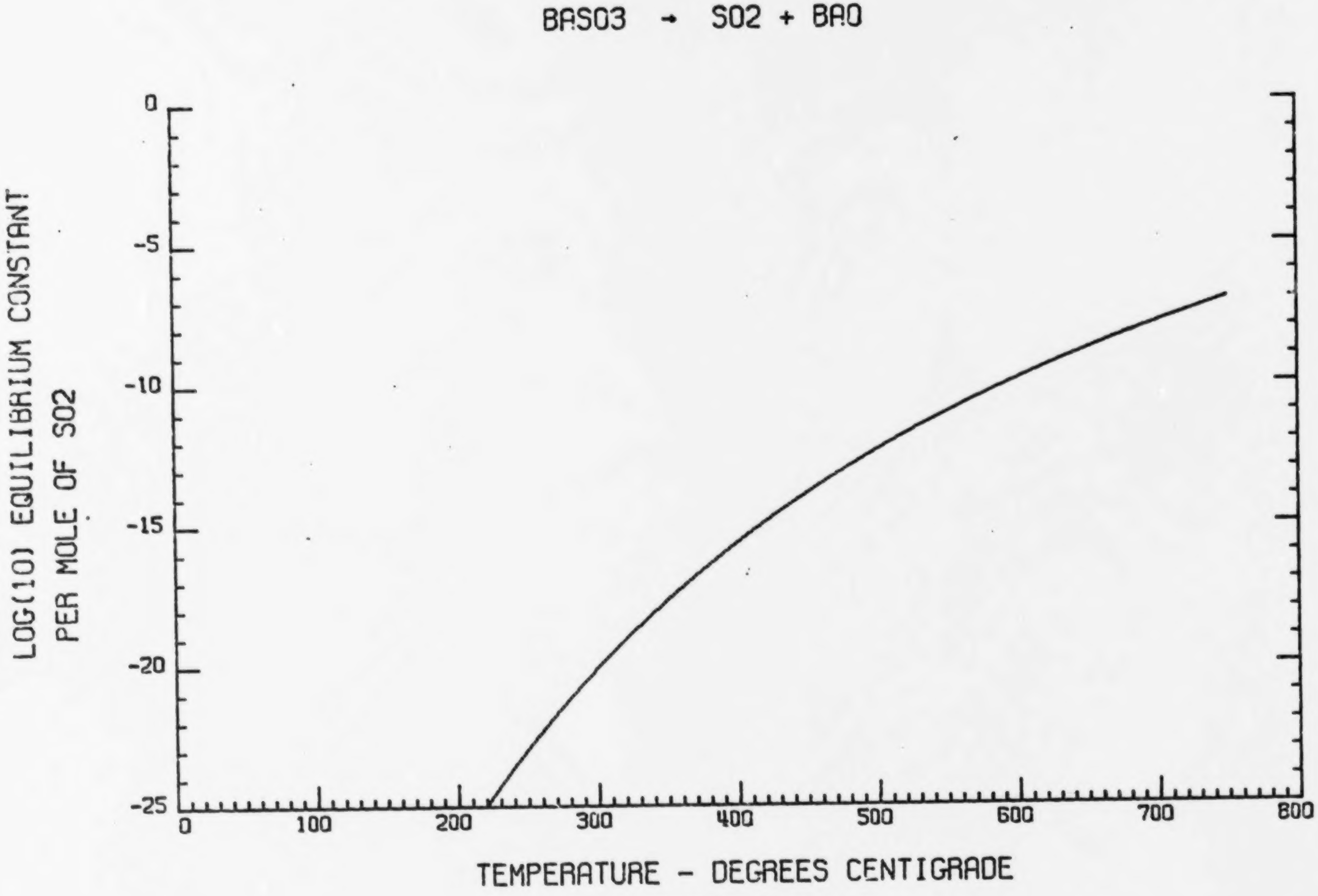


FIGURE 9

26 JUN 68

15) $\frac{1}{2}Zr(SO_3)_2 \rightarrow SO_2 + \frac{1}{2}ZrO_2$ (10)

Sorption: Possible at temperatures < 330° C
Thermal Regeneration: Possible at temperatures > 600° C
(See Figure 10.)

16) Hafnium Sulfite

Estimation of thermodynamic quantities was not possible.

17) Vanadium Sulfite

Value for heat of formation was not estimated. The SO_3 partial pressure of $VOSO_4$ is one atm at 600° C. Based on this fact, one can expect that $VOSO_3$ will not be stable at higher temperatures. However, sorption with formation of $VOSO_3$ will not be possible, because V_2O_5 and V_2O_4 do not react with SO_2 at temperatures < 400° C (See Table 24). This was experimentally confirmed by TRACOR.

18) Niobium Sulfite

19) Tantalum Sulfite

The value for heat of formation could not be estimated, since heats of formation for sulfates or carbonates have not been published.

20) Chromium Sulfite
21) Molybdenum Sulfite
22) Tungsten Sulfite

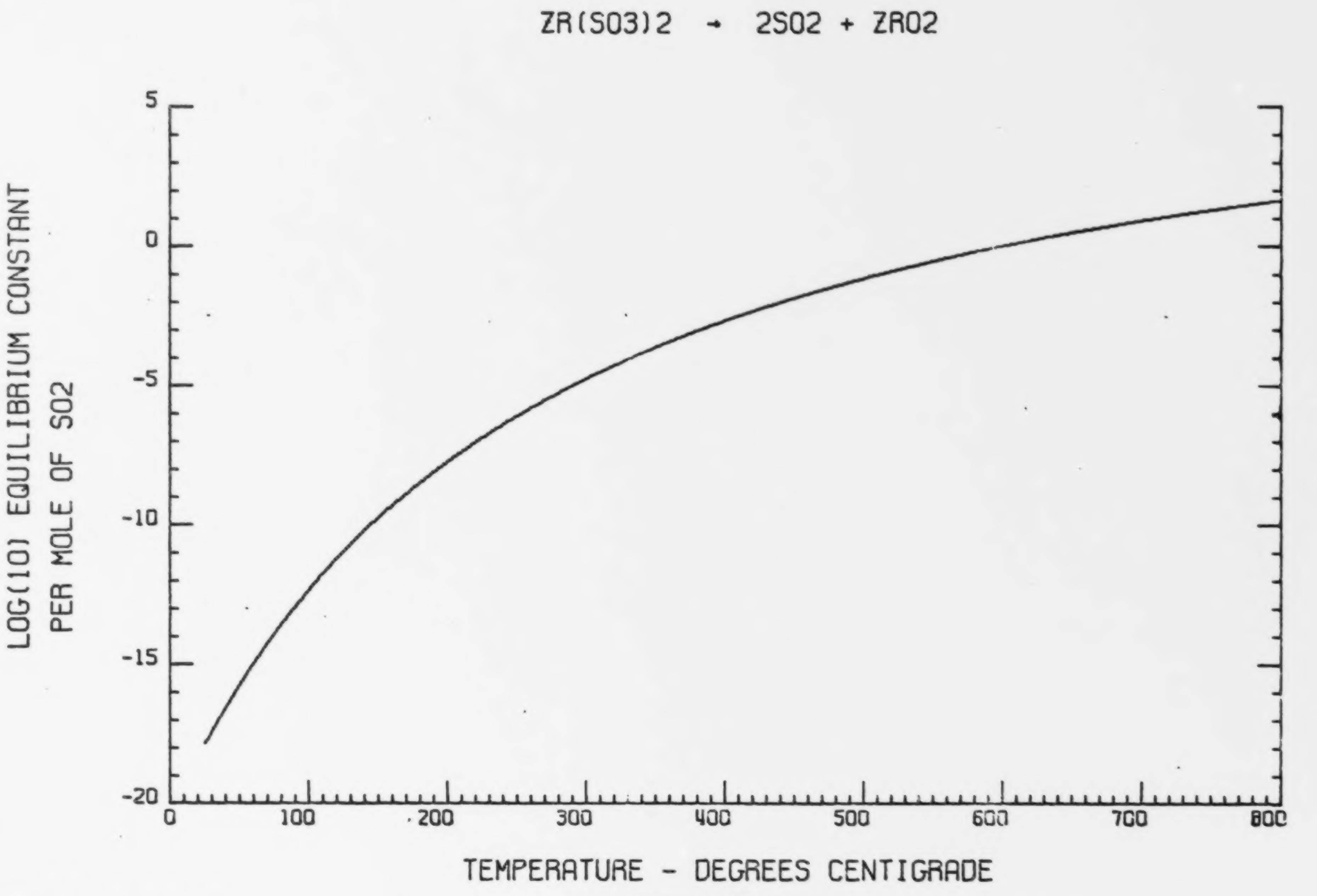

ZR(SO3)2 → 2SO2 + ZRO2
LOG(10) EQUILIBRIUM CONSTANT PER MOLE OF SO2
5
0
-5
-10
-15
-20
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 10

The value for heat of formation could not be estimated. It is known, however, that Cr_2O_3 does not react with SO_2 at temperatures lower than 400° C (see page 132, Section IV). Molybdenum trioxide sublimes at an appreciable rate at temperatures above 600° C.

23) $$MnSO_3 \rightarrow SO_2 + MnO \qquad (11)$$

Sorption: Possible at temperatures $< 240°$ C
Thermal Regeneration: Possible at temperatures $> 440°$ C
(See Figure 11)

24) $$Mn_2(SO_3)_3 \rightarrow 3SO_2 + Mn_2O_3 \qquad (12)$$

Sorption: Possible at temperatures $< 20°$ C
Thermal Regeneration: Possible at temperatures $> 130°$ C
(See Figure 12)

25) Rhenium Sulfite

No calculations were possible. Thermodynamic quantities are given only for the element and some oxides.

26) $$FeSO_3 \rightarrow SO_2 + FeO \qquad (13)$$

Sorption: Possible at temperatures $< 190°$ C
Thermal Regeneration: Possible at temperatures $> 380°$ C.
(See Figure 13)

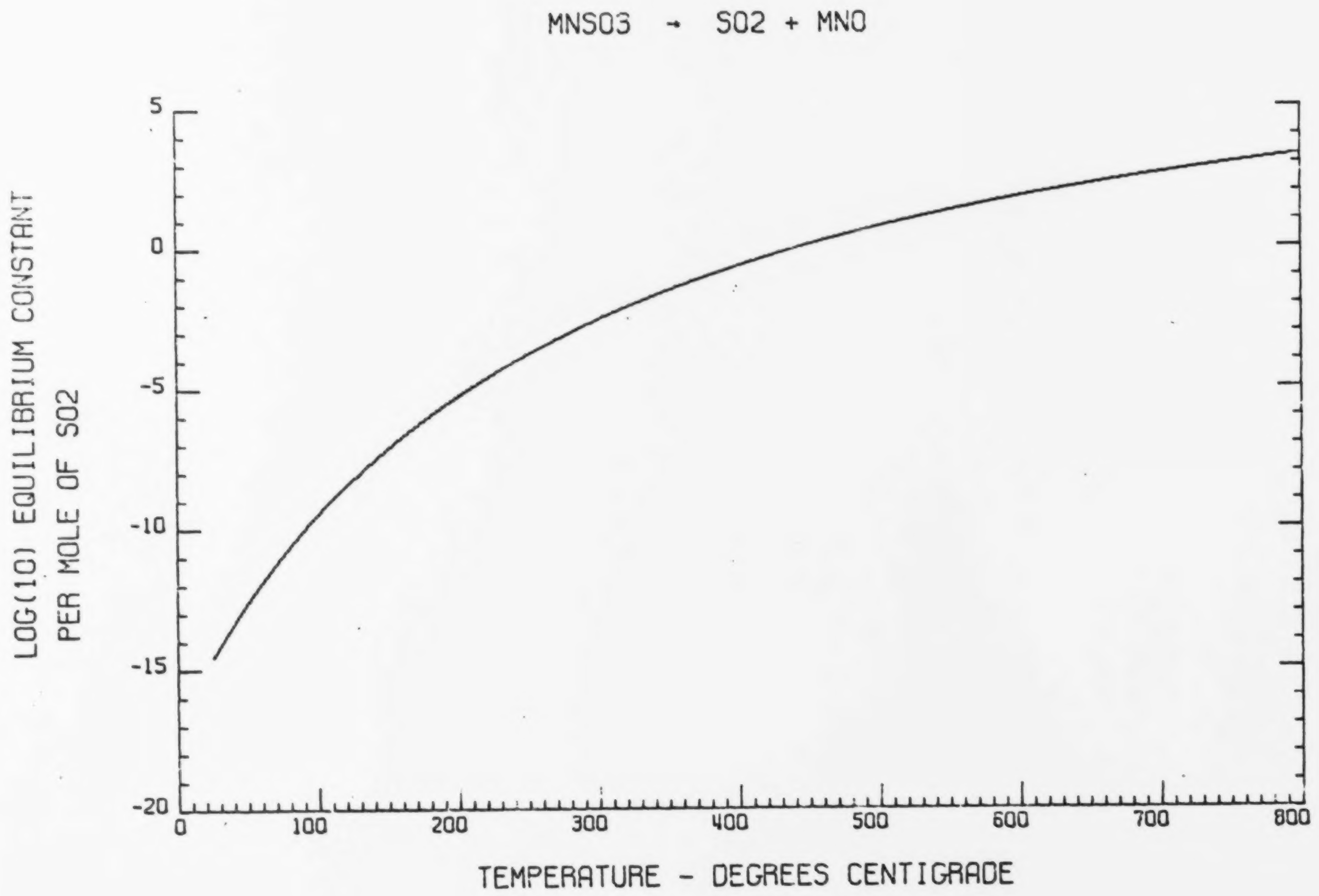


FIGURE 11

17 OCT 68

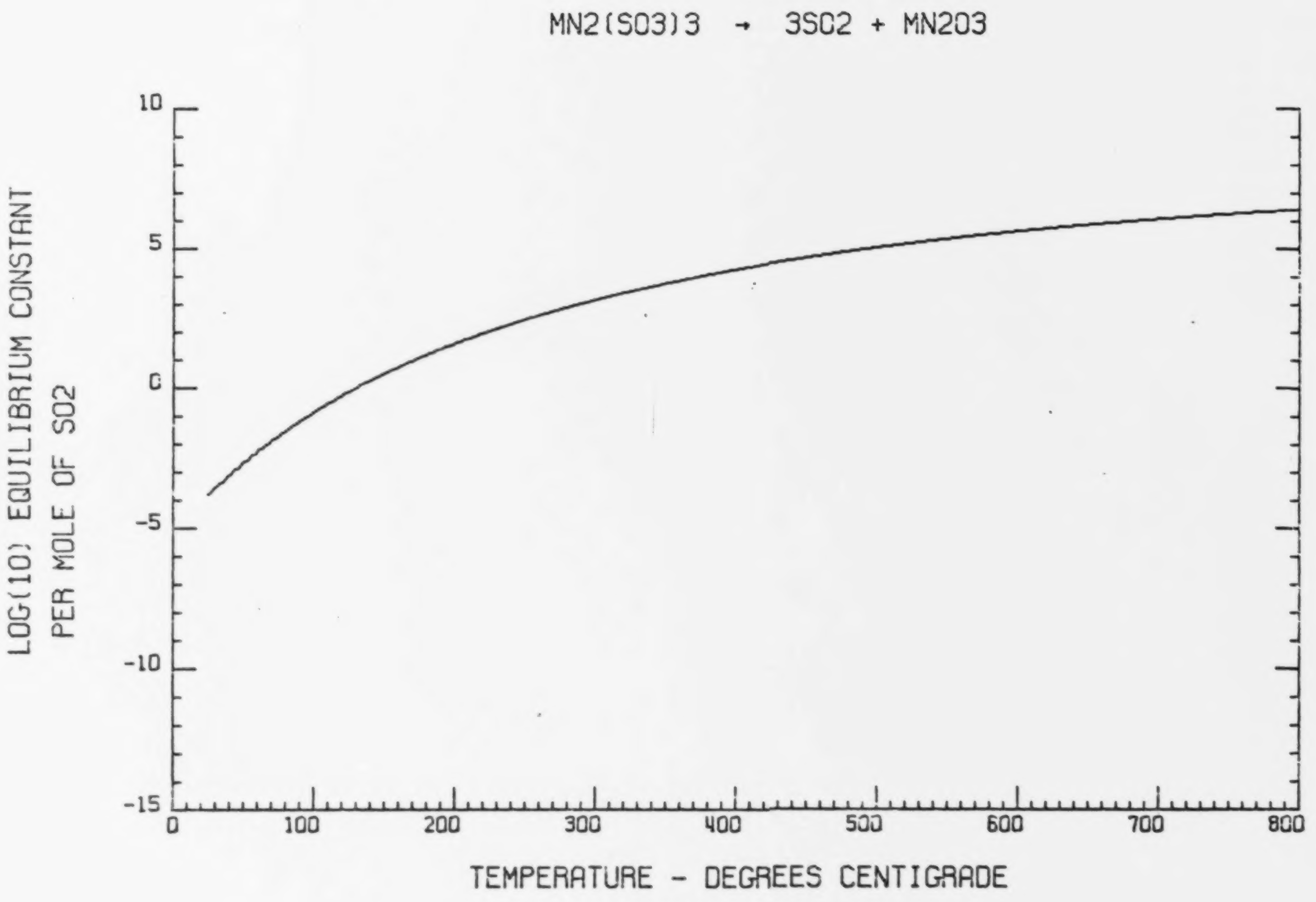

MN2(SO3)3 → 3SO2 + MN2O3
LOG(10) EQUILIBRIUM CONSTANT PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 12

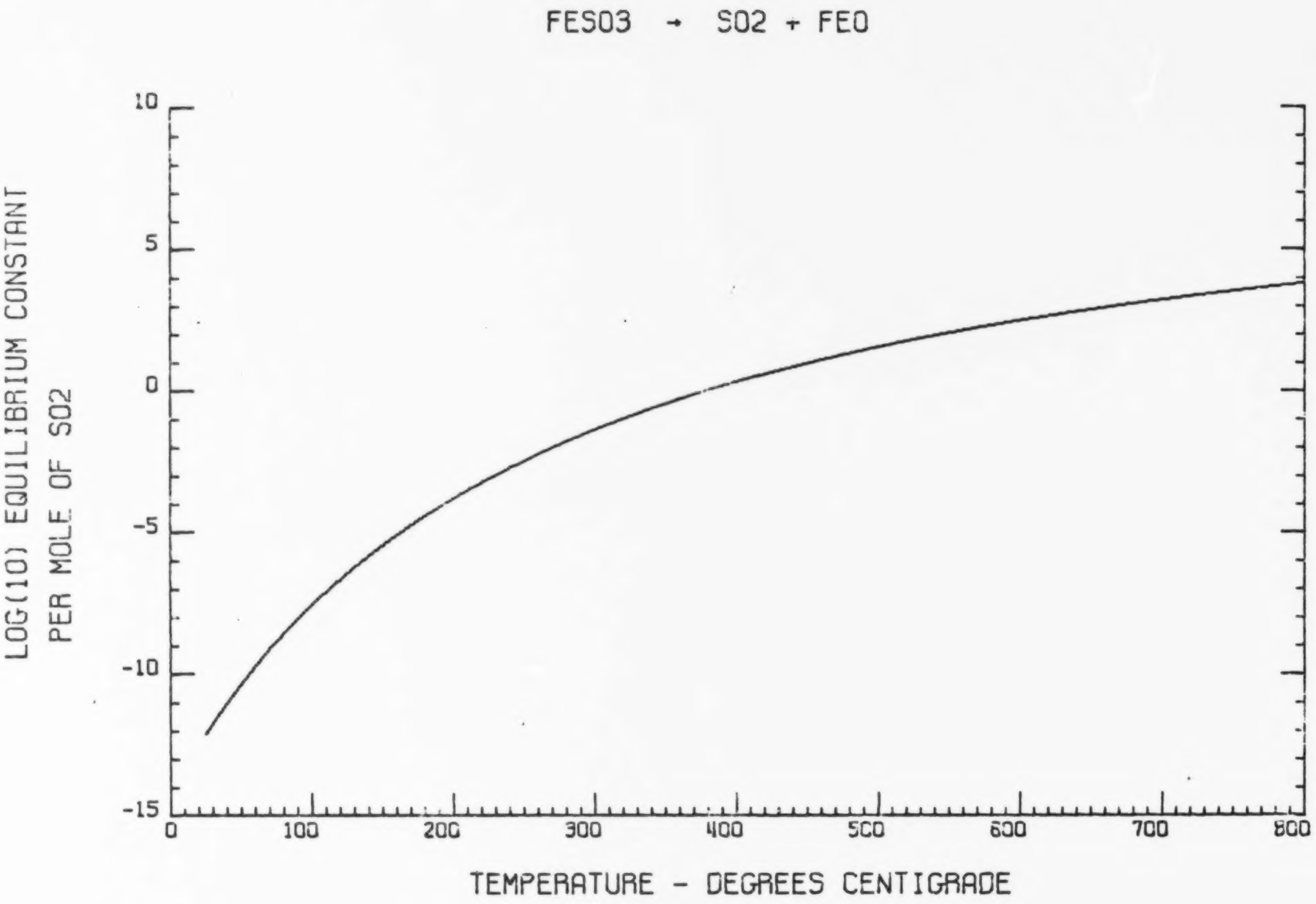

FESO3 → SO2 + FEO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 13

27) $Fe_2(SO_3)_3 \rightarrow 3SO_2 + Fe_2O_3$ (14)

$Fe_2(SO_3)_3$ is unstable at temperatures >60° C.
(See Figure 14)

28) $CoSO_3 \rightarrow SO_2 + CoO$ (15)

Sorption: Possible at temperatures < 250° C
Thermal Regeneration: Possible at temperatures > 470° C
(See Figure 15)

29) $NiSO_3 \rightarrow SO_2 + NiO$ (16)

Sorption: Possible at temperatures < 180° C
Thermal Regeneration: Possible at temperatures > 410° C
(See Figure 16)

30) Rhodium Sulfite
31) Iridium Sulfite
32) Palladium Sulfite

Due to the lack of thermodynamic data, calculations were not possible.

33) $CuSO_3 \rightarrow SO_2 + CuO$ (17)

Sorption: Not possible above 25° C.
(See Figure 17)

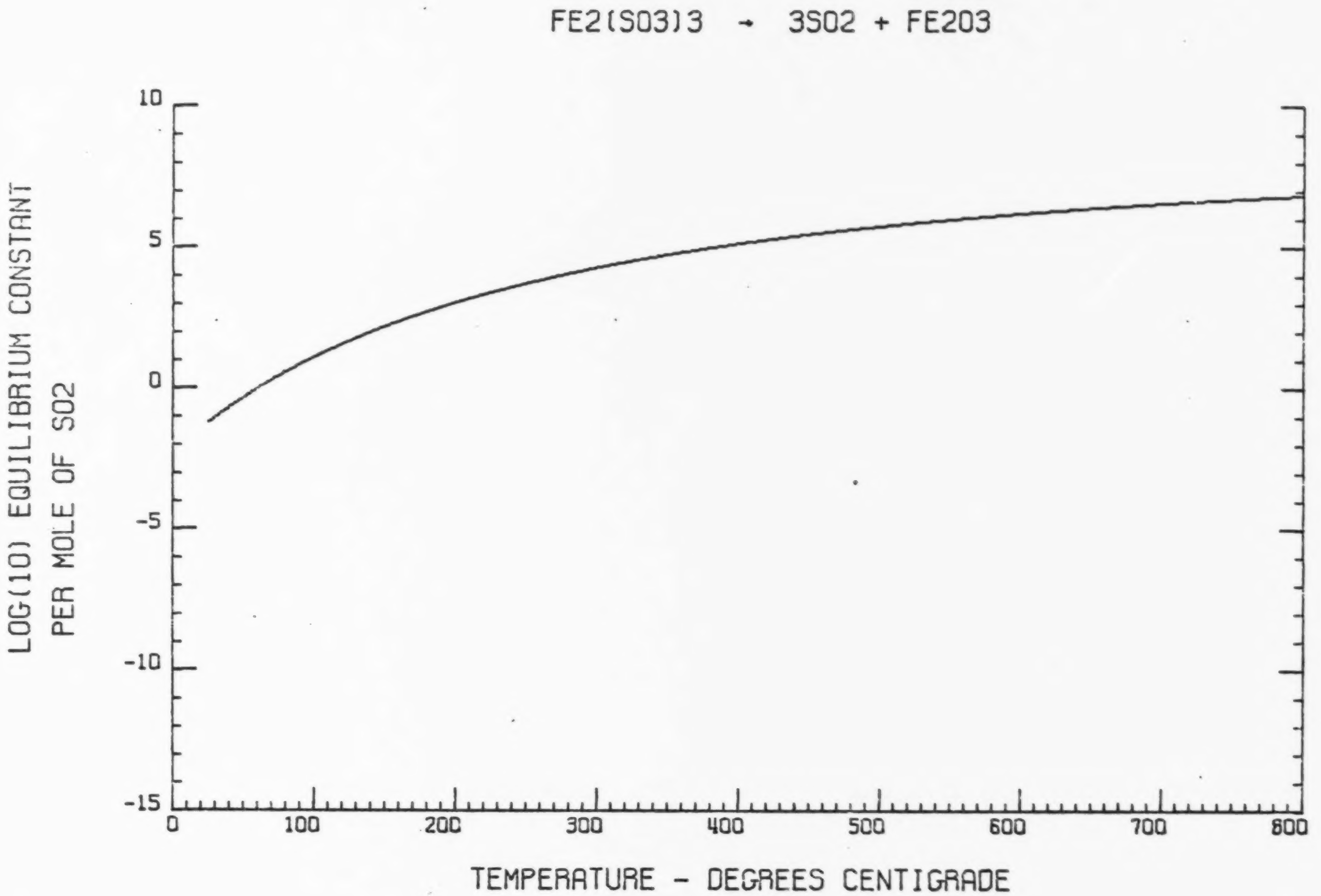

FE2(SO3)3 → 3SO2 + FE2O3
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 14

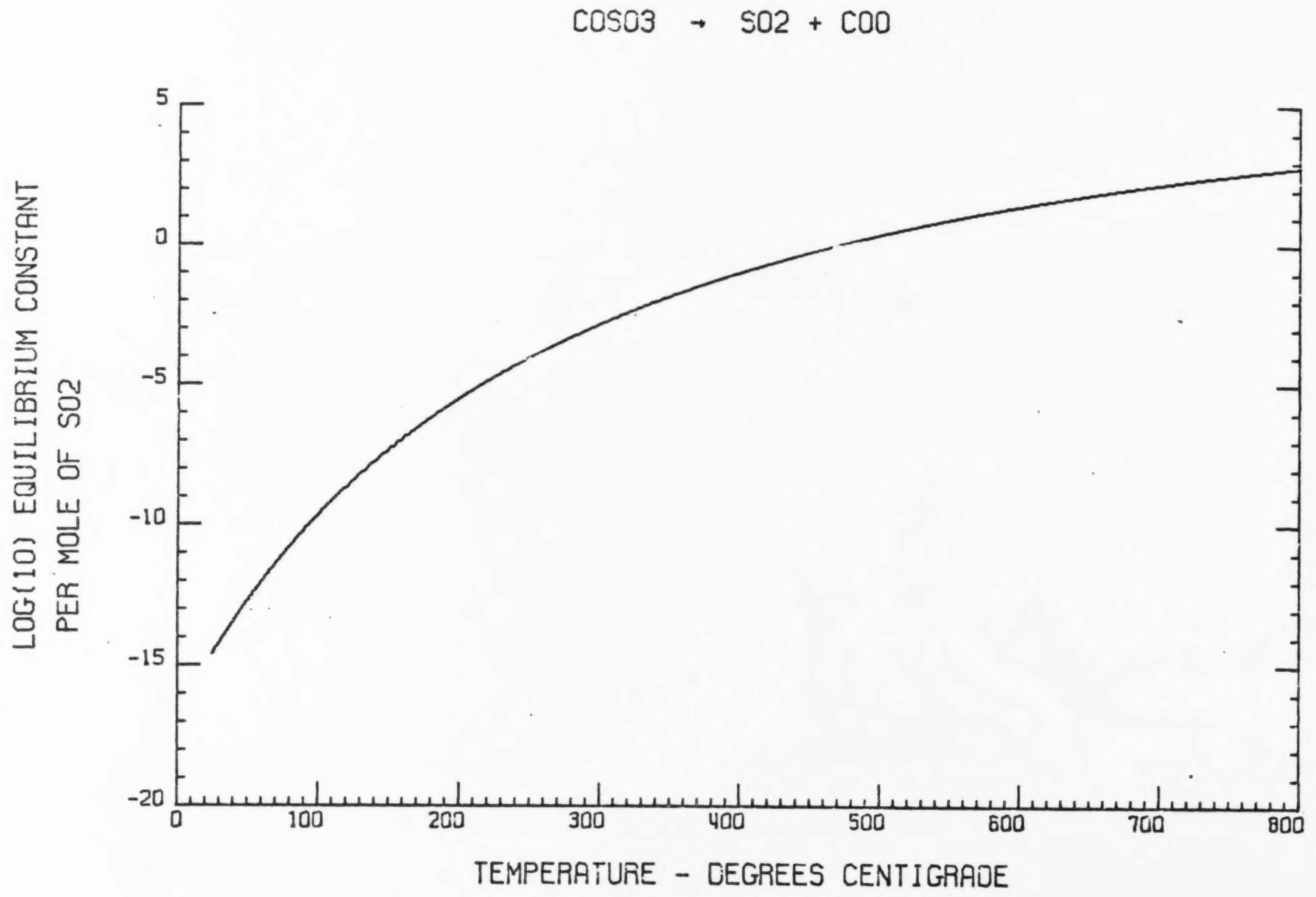

COSO3 → SO2 + COO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
5
0
-5
-10
-15
-20
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 15

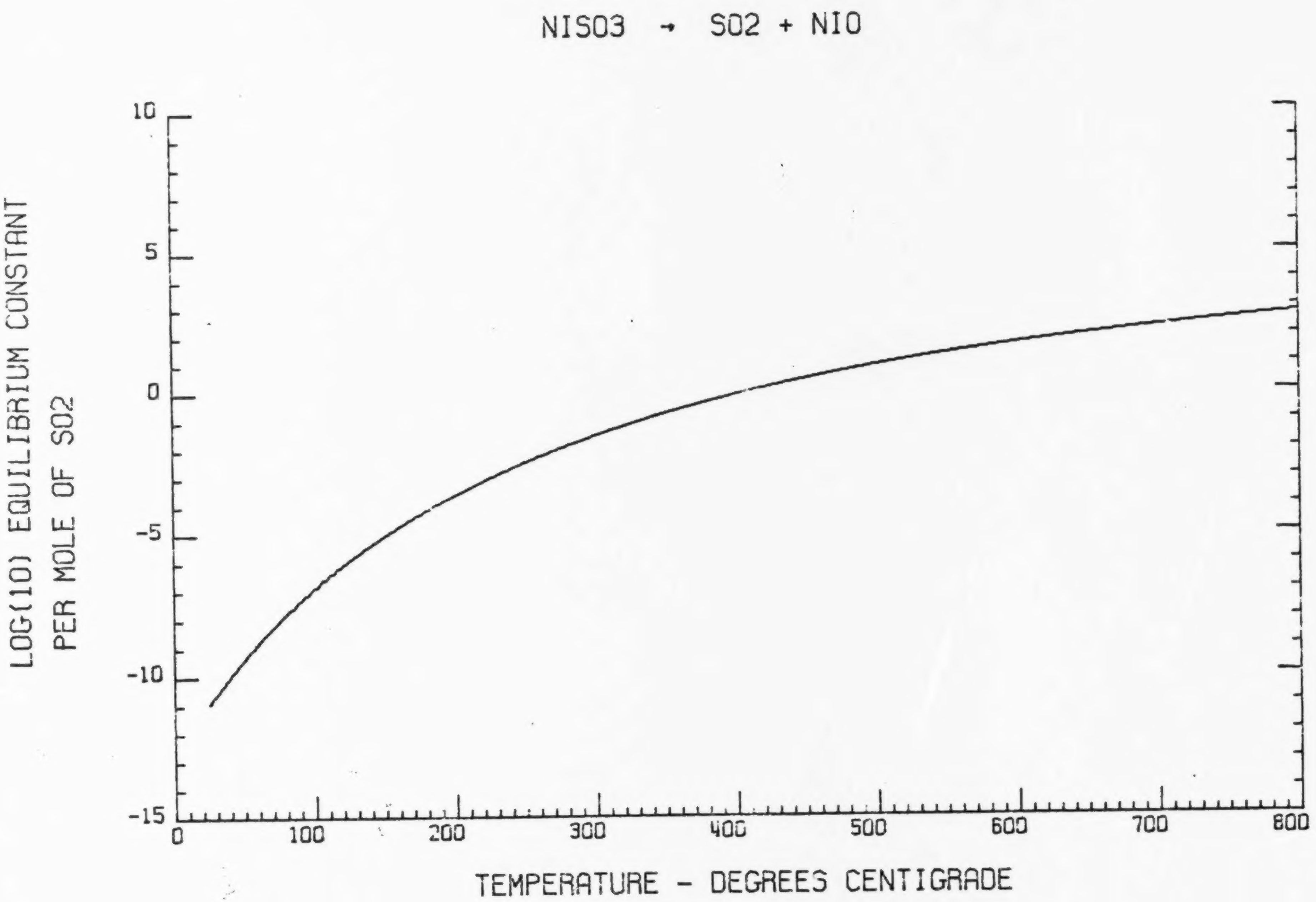

NISO3 → SO2 + NIO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 16

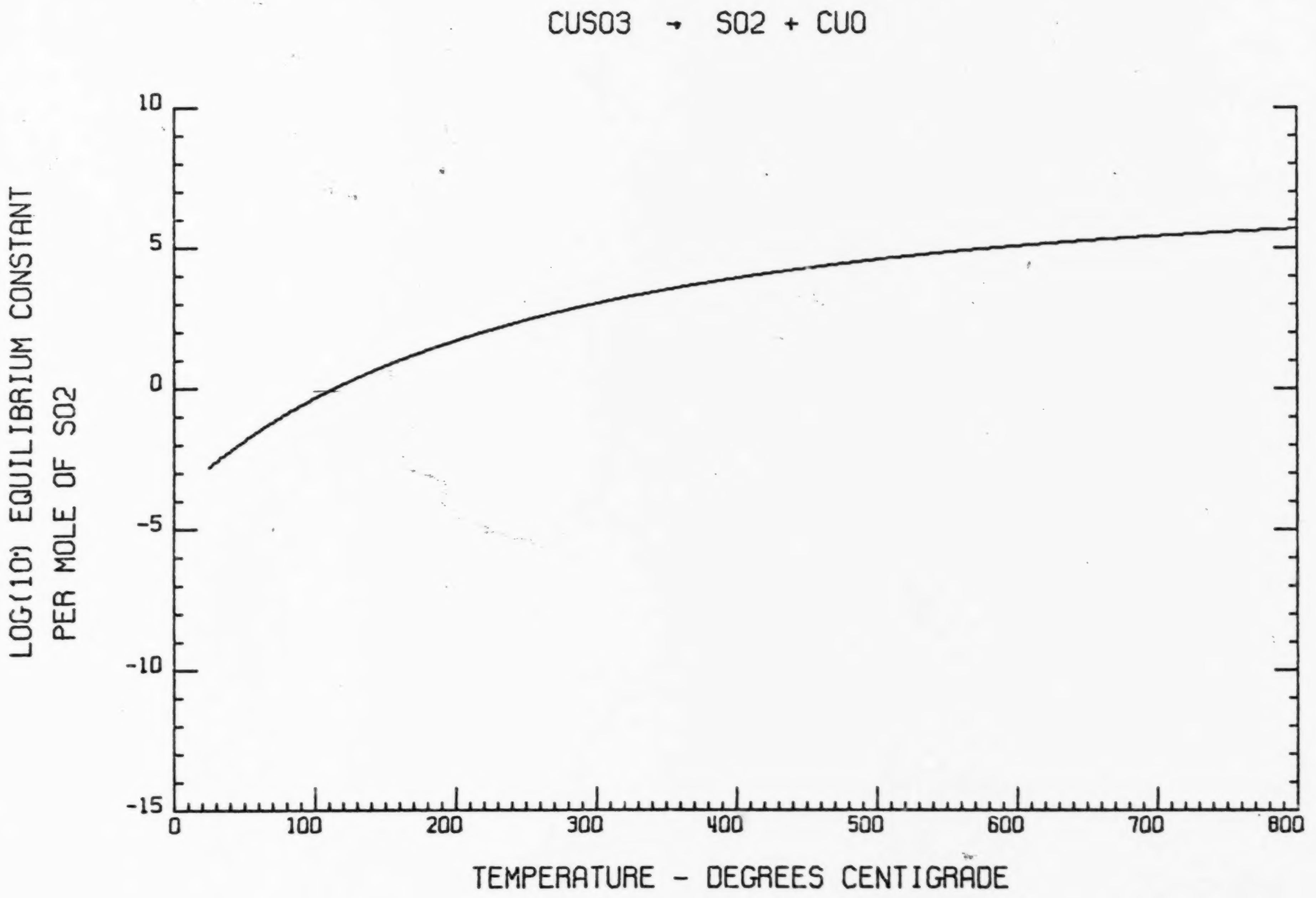

CUSO3 → SO2 + CUO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 17

34) $Cu_2SO_3 \rightarrow SO_2 + Cu_2O$ (18)

Sorption: Not possible above 25° C
(See Figure 18)

35) $Ag_2SO_3 \rightarrow SO_2 + Ag_2O$ (19)

Sorption: Possible at temperatures $< 310°$ C
Thermal Regeneration: Possible at temperatures $> 570°$ C
(See Figure 19)

36) $ZnSO_3 \rightarrow SO_2 + ZnO$ (20)

Sorption: Possible at temperatures $< 110°$ C
Thermal Regeneration: Possible at temperatures $> 290°$ C
(See Figure 20)

37) $CdSO_3 \rightarrow SO_2 + CdO$ (21)

Sorption: Possible at temperatures $< 230°$ C
Thermal Regeneration: Possible at temperatures $> 450°$ C
(See Figure 21)

38) Boron Sulfite

No sulfite, sulfate, or carbonate is known to exist.

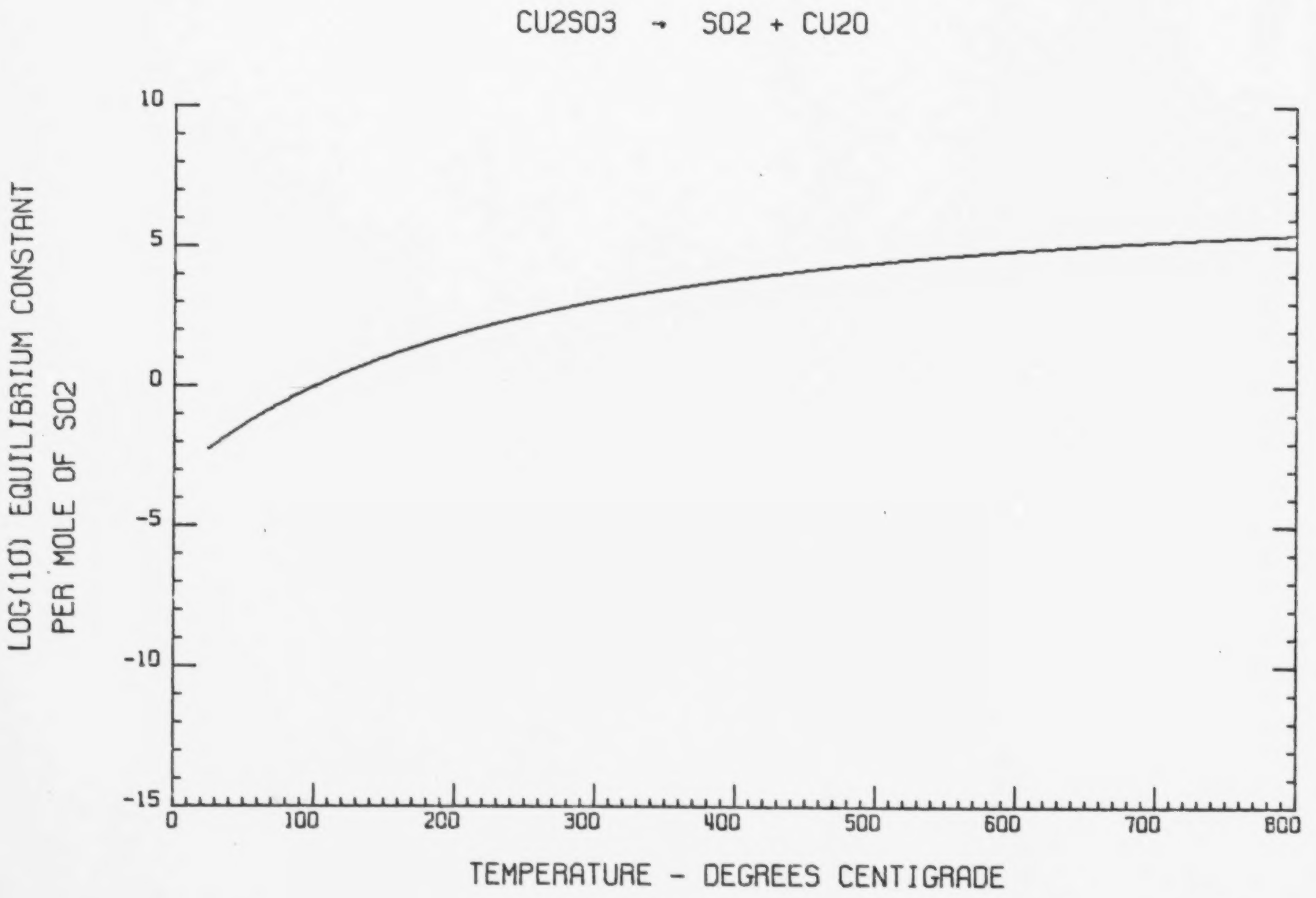


FIGURE 18

29 OCT 68

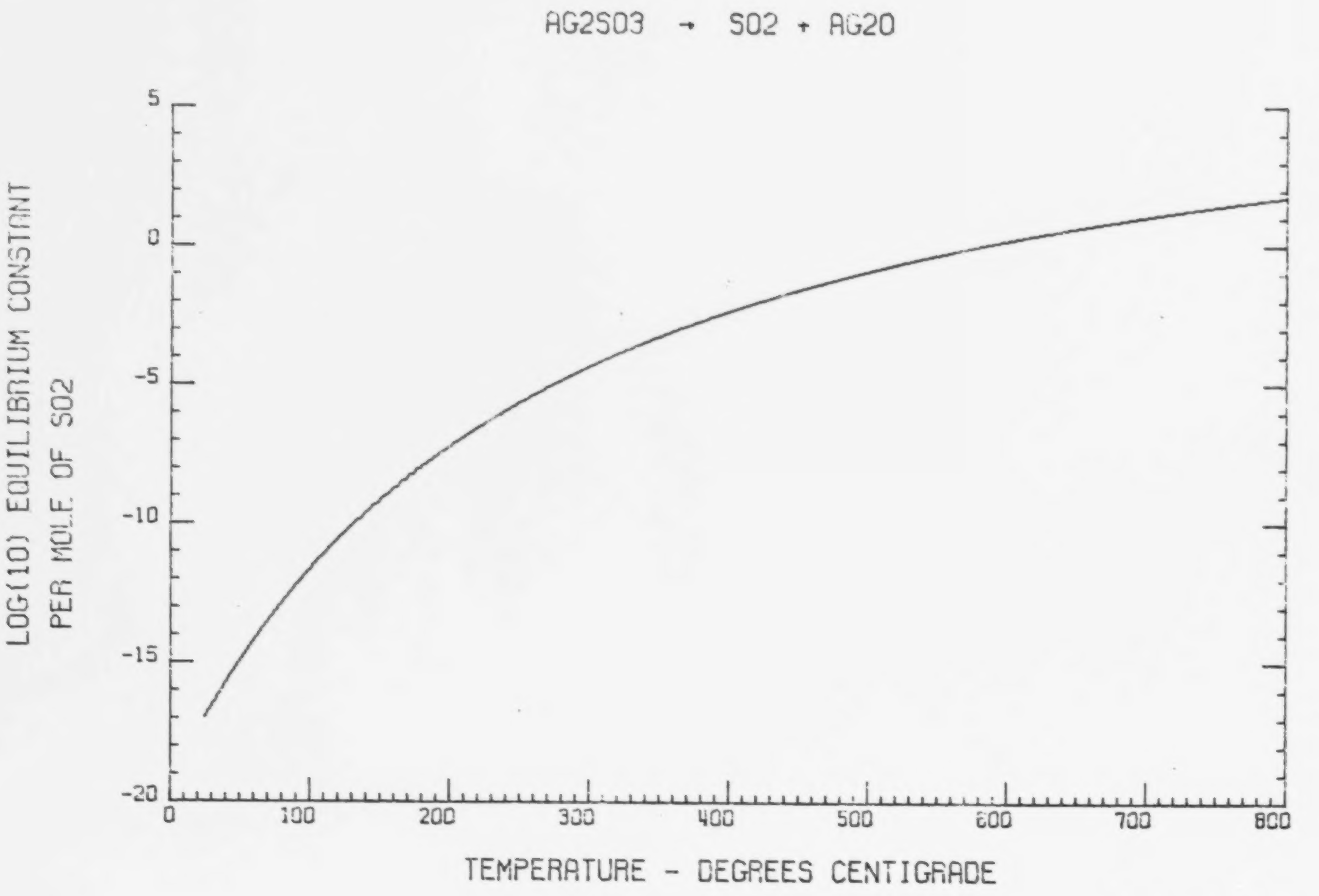

AG2SO3 → SO2 + AG2O
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
5
0
-5
-10
-15
-20
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 19

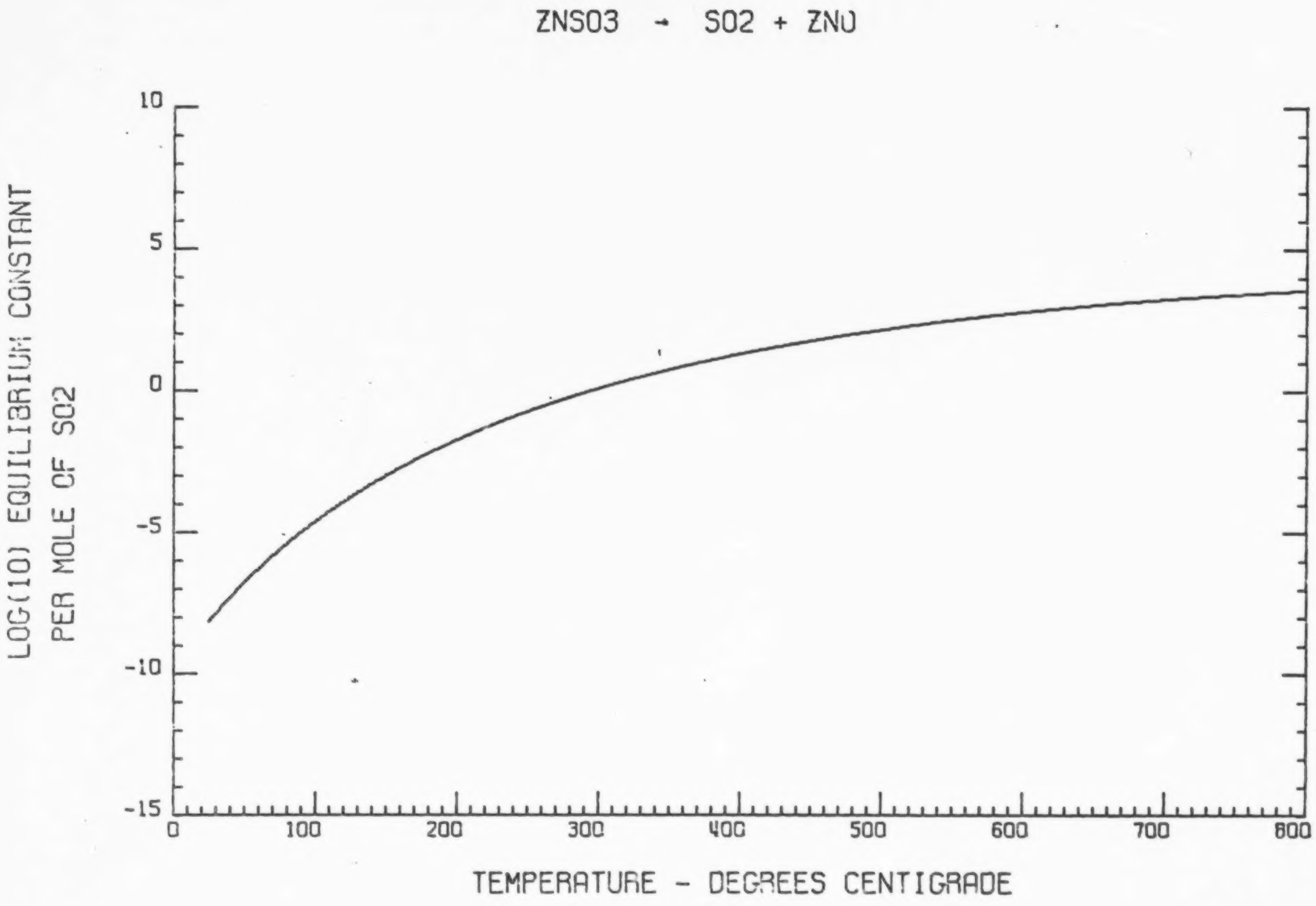

ZNSO3 → SO2 + ZNO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 20

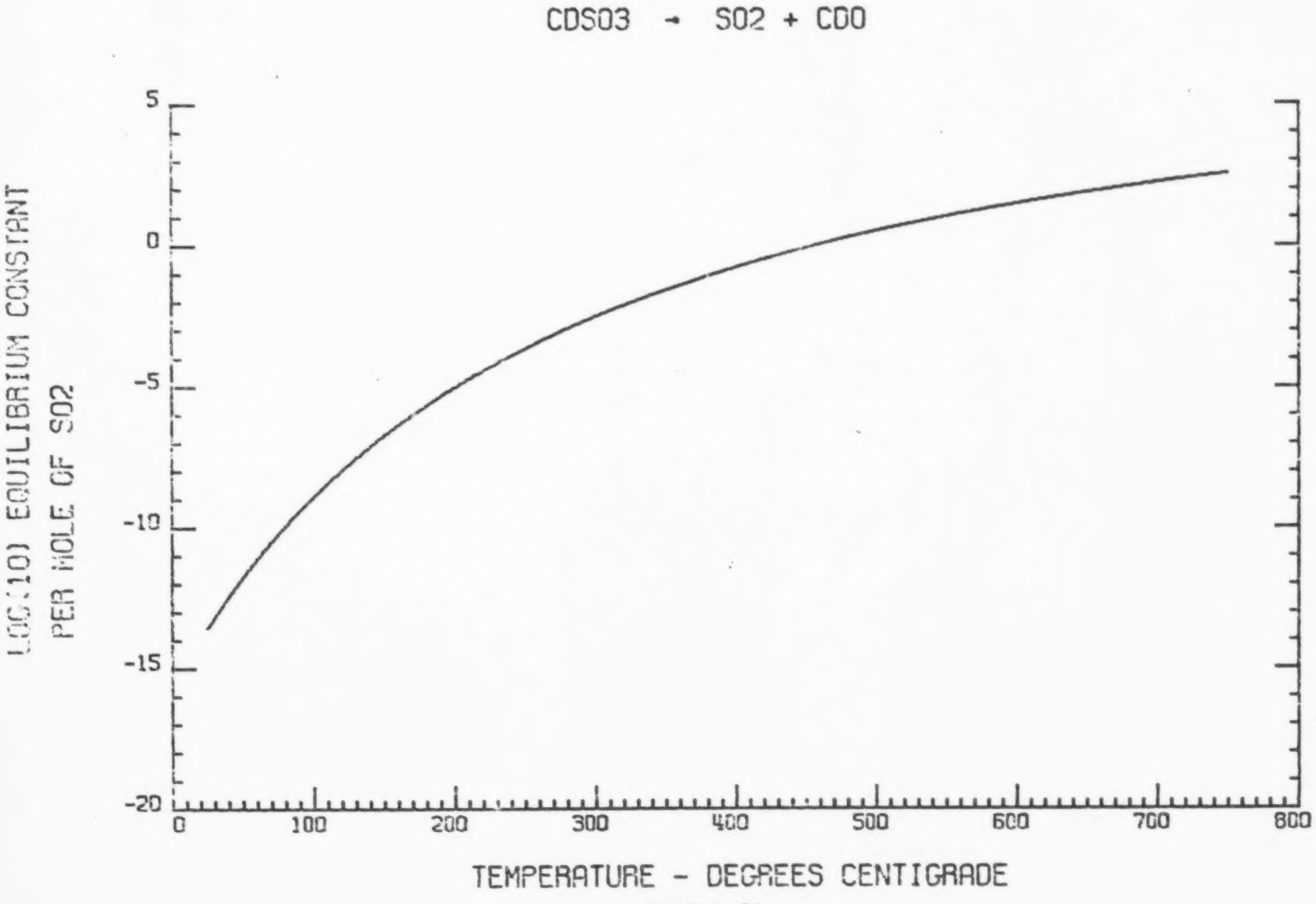


FIGURE 21

27 JUN 68

39) $Al_2(SO_3)_3 \rightleftarrows 3SO_2 + Al_2O_3$ (22)

* (See Figure 22)

40) Gallium Sulfite

Thermodynamic data are not available.

41) Silicon Sulfite

Silicon sulfates or carbonates are unknown.

42) Germanium Sulfite

Thermodynamic data are not available.

43) $Sn(SO_3)_2 \rightarrow 2SO_2 \rightarrow SnO_2$ (23)
Sorption: Not possible above 25° C
(See Figure 23)

* According to Figure 22, anhydrous $Al_2(SO_3)_3$ is unstable at temperatures higher than 70° C. This is in good agreement with the data given by W. Machu (MA-004) who observed that monobasic aluminum sulfite is stable up to 100° C. P. V. Dibina (DI-001) investigated the decomposition behavior of aluminum sulfite. SO_2 evolution was reported to occur in the 200-300° C range. He observed the formation of polybasic sulfites which retain traces of SO_2 up to 500-600° C.

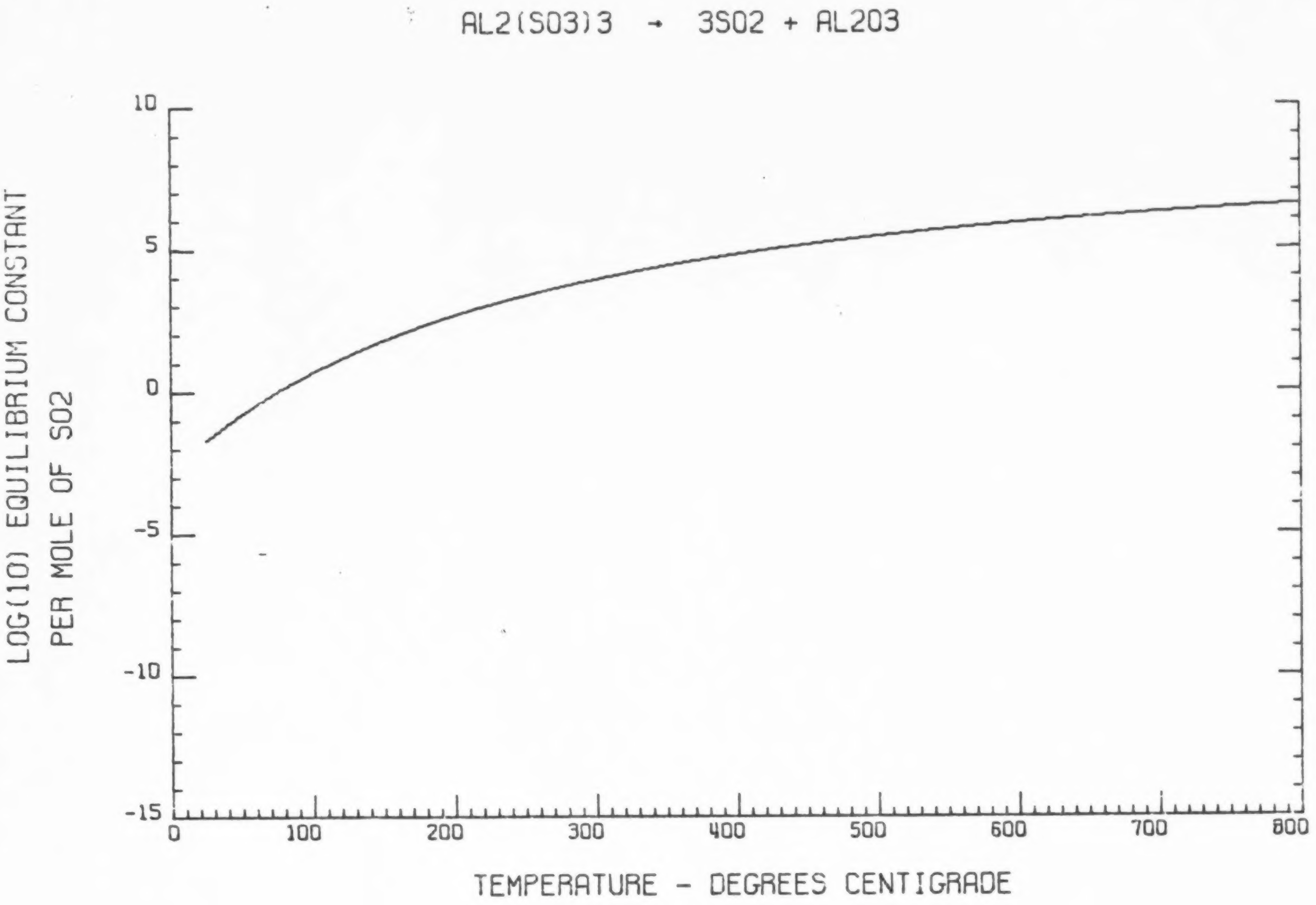


FIGURE 22

12 DEC 68

TRACOR

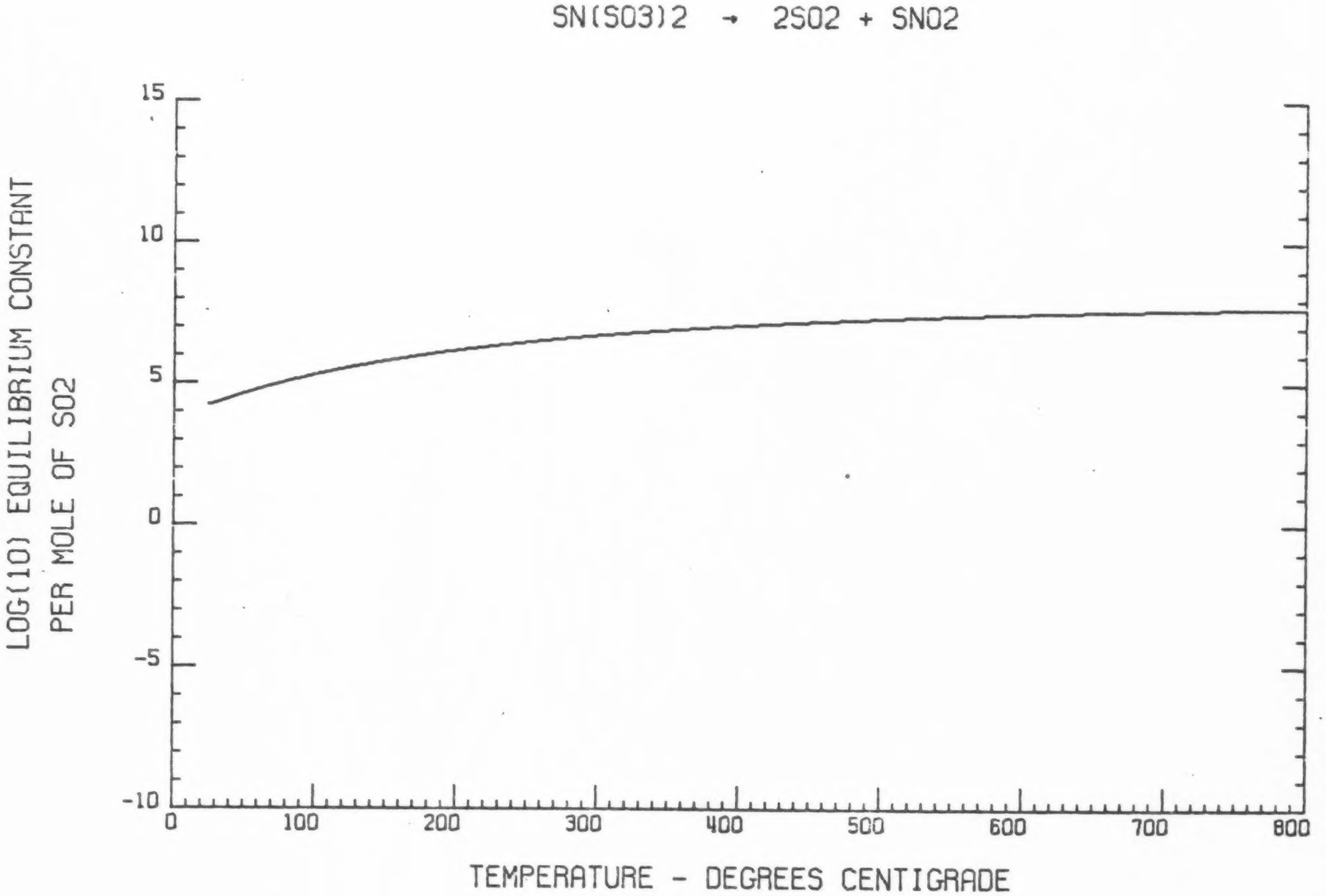


FIGURE 23

17 OCT 68

44) $PbSO_3 \rightarrow SO_2 + PbO$ (24)

Sorption: Possible at temperatures < 330° C
Thermal Regeneration: Possible at temperatures > 600° C
(See Figure 24)

45) Arsenic Sulfite

Arsenic sulfite, sulfate, or carbonate is unknown.

46) $Sb_2(SO_3)_3 \rightarrow 3SO_2 + Sb_2O_3$ (25)

Sorption: Not possible above 25° C
(See Figure 25)

47) $Bi_2(SO_3)_3 \rightarrow 3SO_2 + Bi_2O_3$ (26)

Sorption: Possible at temperatures < 150° C
Thermal Regeneration: Possible at temperatures > 310° C
(See Figure 26)

48) $U(SO_3)_2 \rightarrow 2SO_2 + UO_2$ (27)

Sorption: Possible at temperatures < 130° C
Thermal Regeneration: Possible at temperatures > 320° C
(See Figure 27)

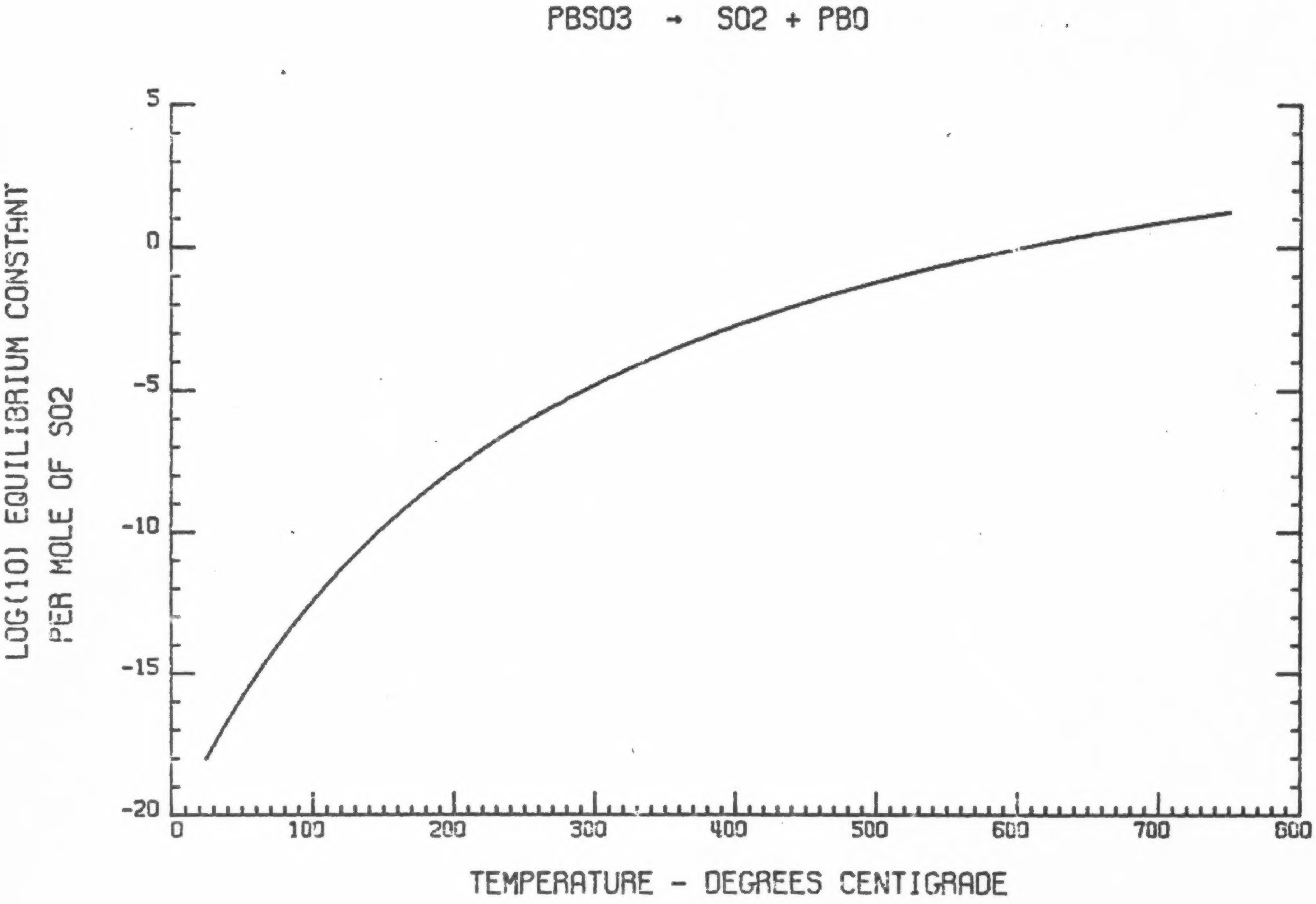

PBSO3 → SO2 + PBO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
5
0
-5
-10
-15
-20
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 24

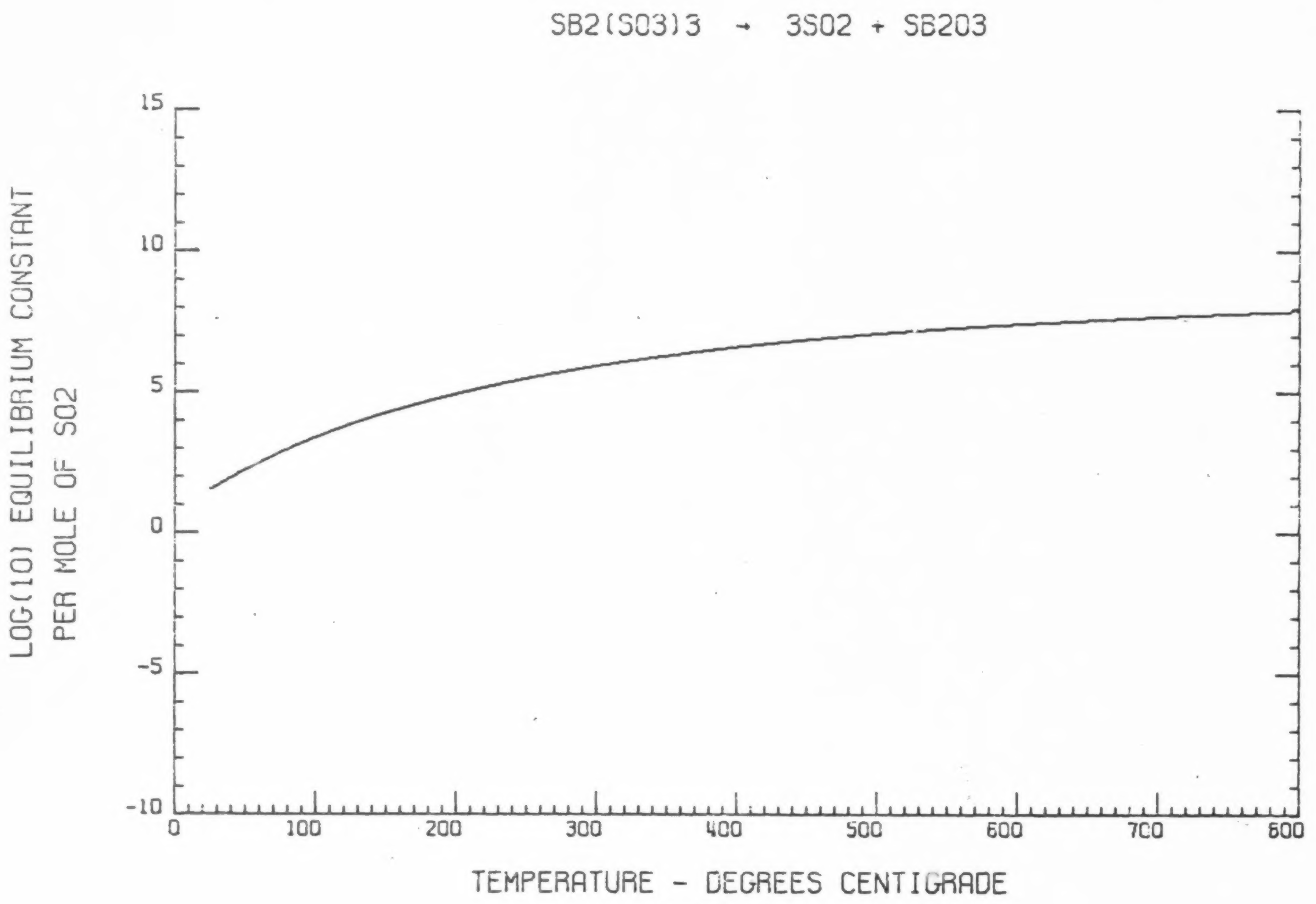

SB2(SO3)3 → 3SO2 + SB2O3
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 25

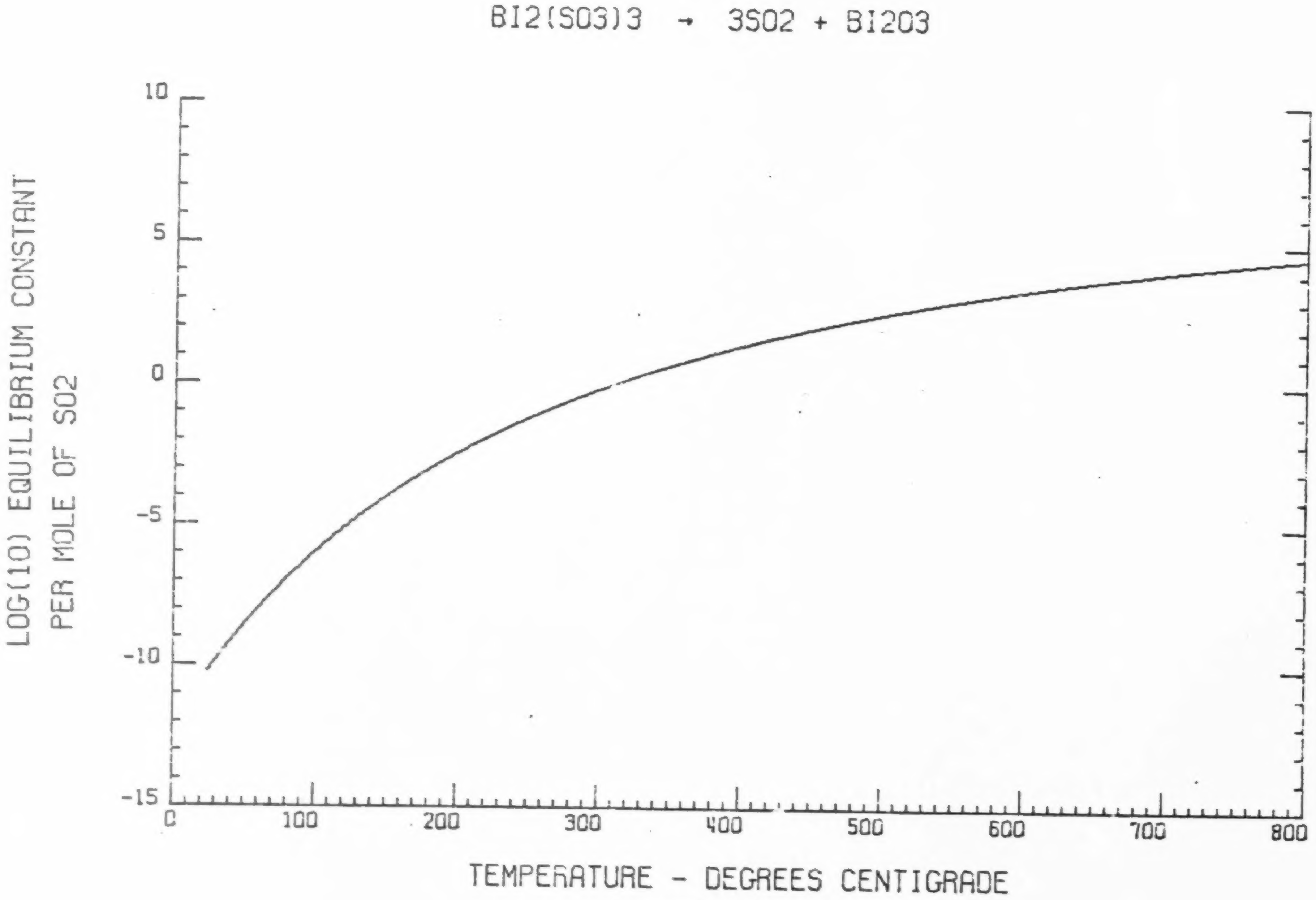

BI2(SO3)3 → 3SO2 + BI2O3
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 26

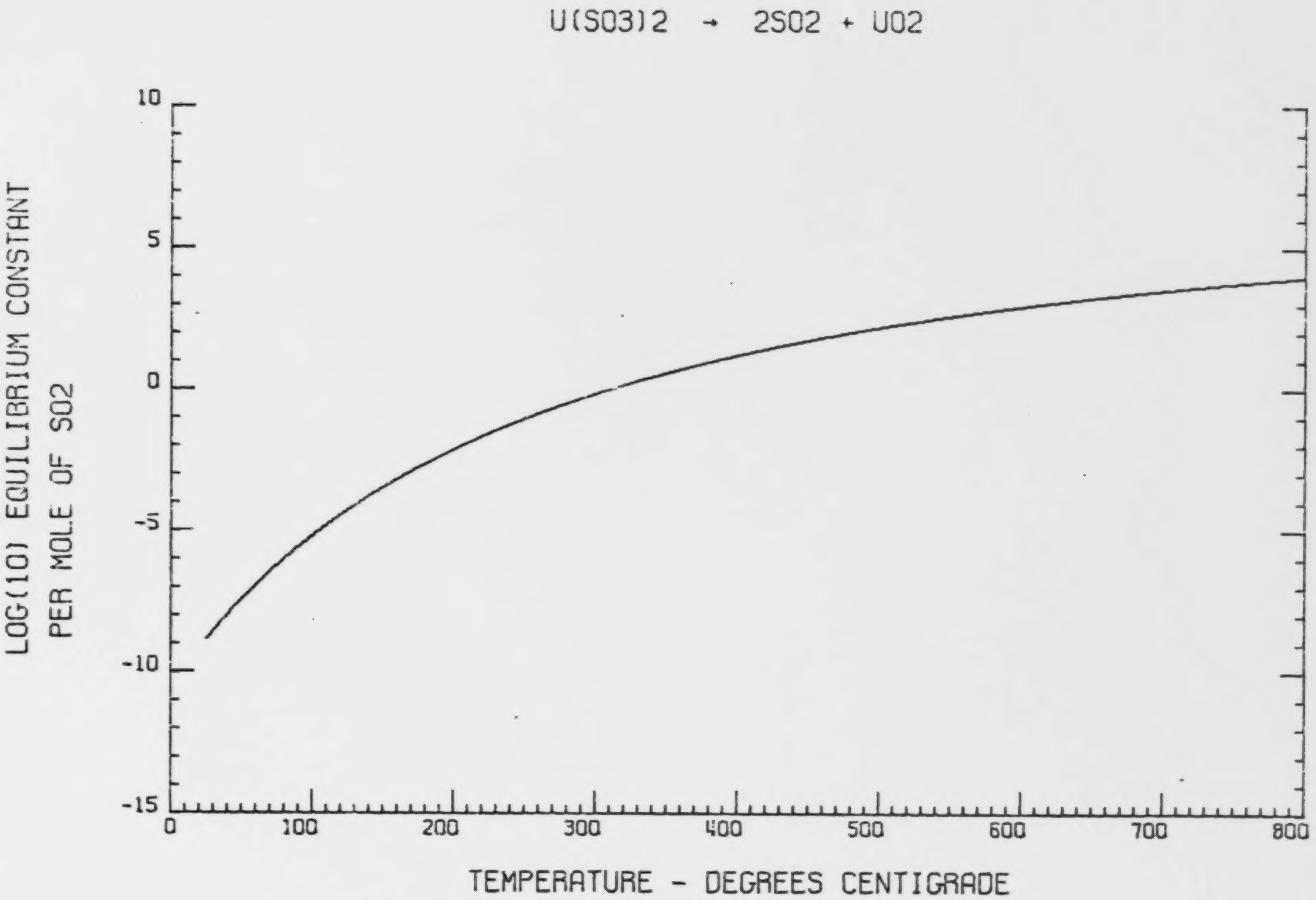

U(SO3)2 → 2SO2 + UO2
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 27

49) $Th(SO_3)_2 \rightarrow 2SO_2 + ThO_2$ (28)

Sorption: Possible at temperatures < 190° C
Thermal Regeneration: Possible at temperatures > 390° C
(See Figure 28)

The conclusions of the applicability of sulfite processes are summarized in Section V.

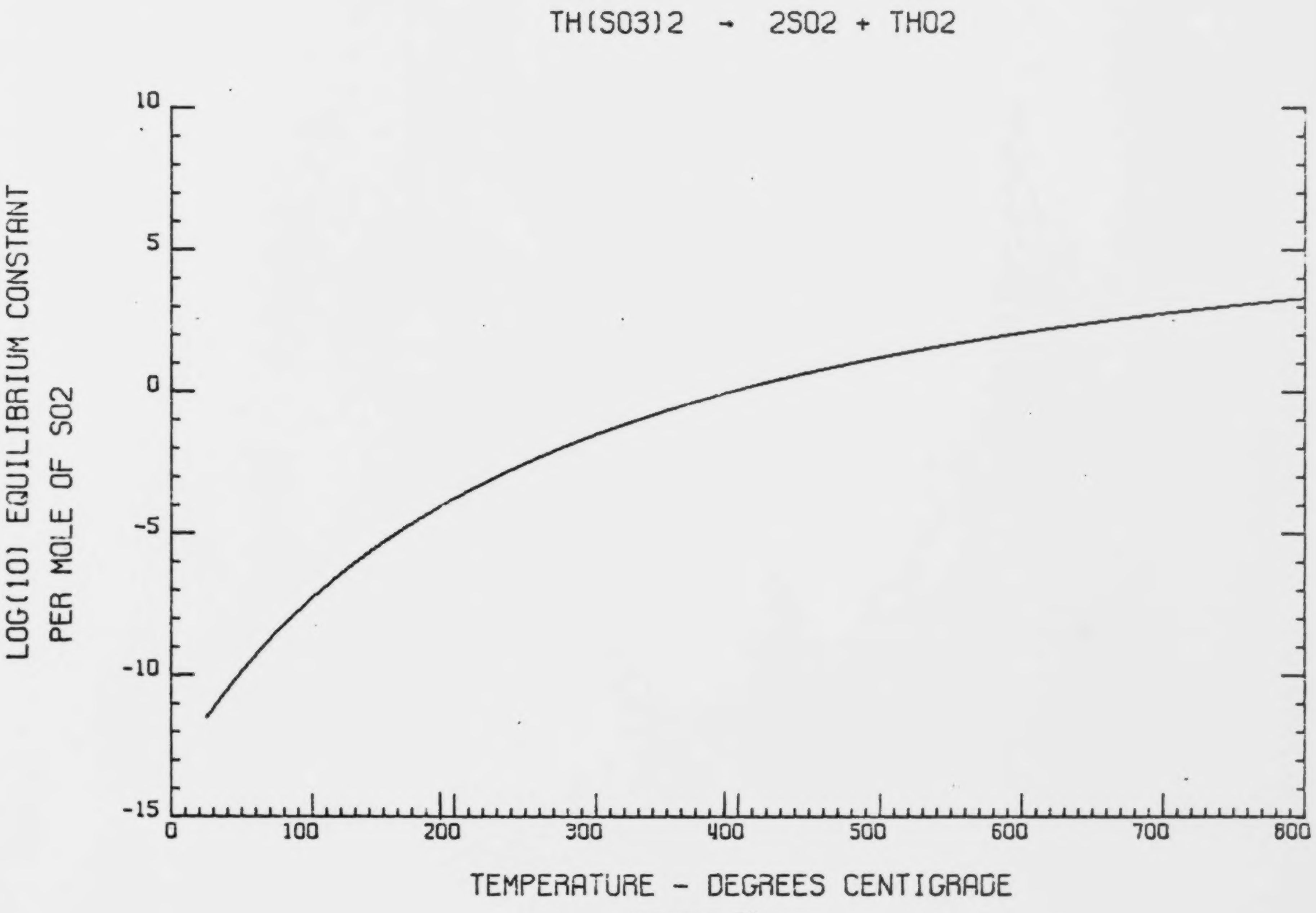

TH(SO3)2 → 2SO2 + THO2
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO2
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 28

B. The Disproportionation and Decomposition of the Sulfites

According to Castellani and Co-workers (CO-003, CO-004, CO-005, GA-001, CL-001) and Trautz and Paksckwer (TR-011), the sulfites can be divided into three groups.

a) K_2SO_3, Na_2SO_3, and Li_2SO_3 disproportionate almost entirely into sulfides and sulfates.

b) Ca, Ba, Sr, Zn, Cd, Pb, Mn, La, Sm, and Tl sulfites show both disproportionation and decomposition. While the phase rule combined with thermodynamic calculations usually predicts complete disproportionation, the kinetics of this reaction are slow enough that the material may be heated to the decomposition point.

c) Ag_2SO_3 and Hg_2SO_3 decompose with formation of metal, SO_2, and sulfate.

In experiments performed in an inert atmosphere, the molar ratio sulfate-sulfur/sulfide-sulfur in the residue was found to be nearly three. The formation of thiosulfate as an intermediate was confirmed in the decomposition behavior of magnesium sulfite where MgS_2O_3 could be identified in the residue (FO-001). This indicated that the following mechanism occurred:

$$4MeSO_3 \rightarrow 2MeSO_4 + 2MeSO_2 \qquad (29)$$

$$2MeSO_2 \rightarrow MeS_2O_3 + MeO \qquad (30)$$

$$\underline{MeO + MeS_2O_3 \rightarrow MeSO_4 + MeS} \qquad (31)$$

$$4MeSO_3 \rightarrow 3MeSO_4 + MeS \qquad (32)$$

The reaction in Equation 32 is nonvariant. The equilibrium is favored in one direction until one component is consumed. For lower temperatures the equation is shifted to the right as the calculations to be described later indicate. However, when the decomposition temperature of the sulfite is reached the following reaction occurs (FO-001):

$$3MeSO_4 + MeS \rightarrow 4MeO + SO_2 \qquad (33)$$

This reaction is univariant. This means that at the temperature where p_{SO_2} of the sulfite is greater than the P_{SO_2} of the gas atmosphere, Equation 32 is shifted to the left, and the resulting sulfite decomposes. The overall reaction is shown by Equation 33. This was confirmed experimentally by Trautz and Pakschwer (TR-011, FO-001). Therefore, it is understandable that the alkali sulfites with a high decomposition temperature show complete disproportionation. The other sulfites investigated, with decomposition temperatures lower than that of the alkali metal sulfites, show both disproportionation and decomposition. The figures in Section II-B, show that the decomposition becomes more important the lower the decomposition temperature of the sulfite.

A modification of the reaction in Equation 33 was used in Germany during World War I to produce sulfur and cement from calcium sulfate. There are several patents which describe the process (DE-002, DE-003, DE-004, DE-005). The process was carried out according to the reaction in Equation 33a.

$$CaSO_4 + 4C \rightarrow CaS + 4CO \qquad (33a)$$

At 1000-1100°C the rate of this reaction is appreciable. CaS reacts in this temperature range with $CaSO_4$ according to Equation 33b.

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2 \qquad (33b)$$

The ingredients normally used in cement production, for instance koalin, can be added along with the carbon. The following side reactions are predicted:

$$2SO_2 + 4C \rightarrow 4CO + S_2 \qquad (33c)$$

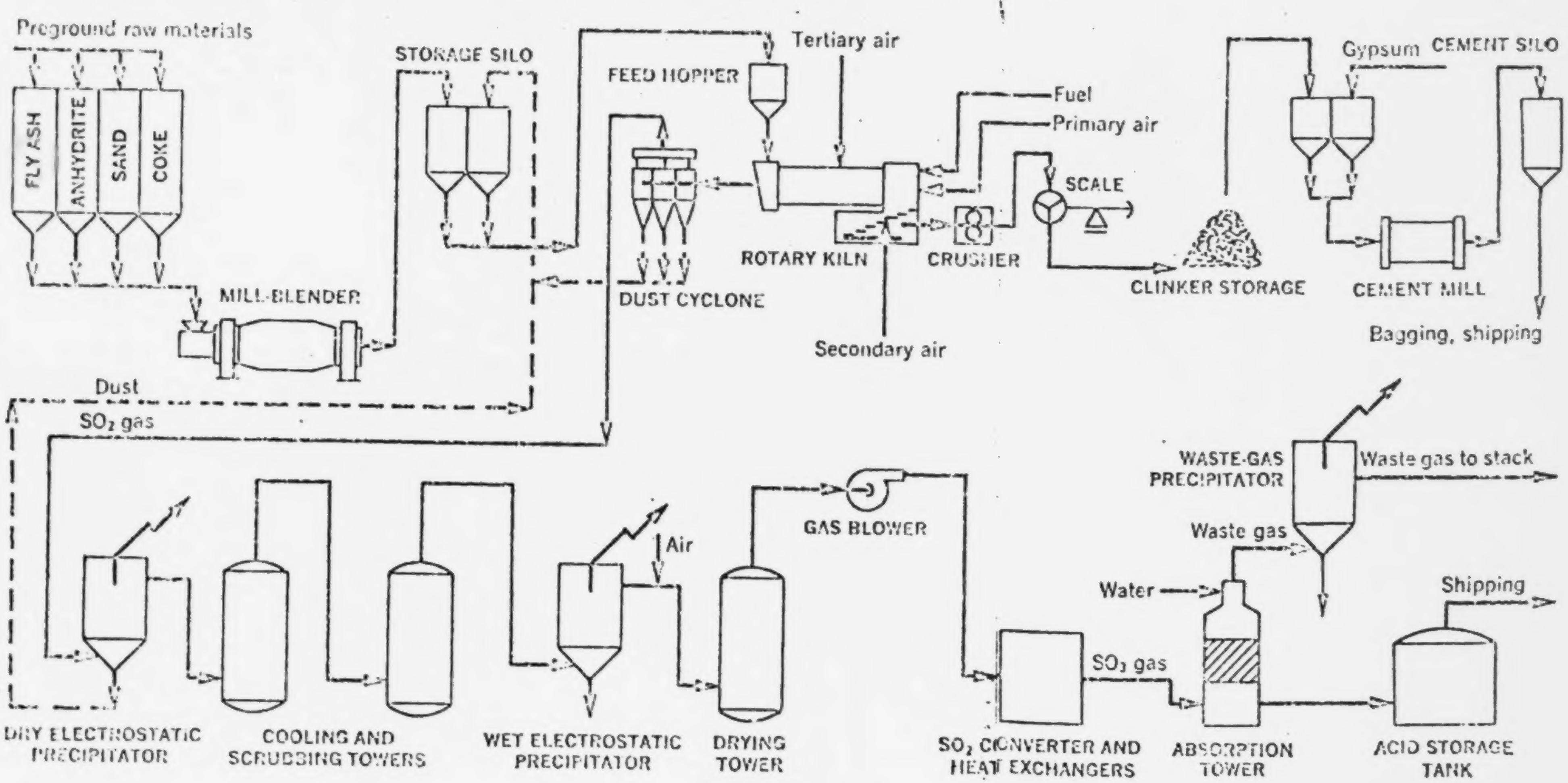
$$2SO_2 + 4CO \rightarrow 4CO_2 + S_2 \qquad (33d)$$

The end products are therefore cement, SO_2 and S_2. This process may become attractive as soon as the limestone injection process is in a more advanced stage of development. The flow diagram on the following page was published by the Österreichische Stickstoffwerke A. G., Linz (RE-004). Instead of natural gypsum, the $CaSO_4$ formed in the limestone injection process could be used.

The disproportionation reaction is not characteristic of the sulfites only. The tendency to disproportionate is also known for other compounds. For example,

Chlorates → Perchlorate + Chloride

Phosphites and Hypophosphites → Phosphide + Phosphate


Preground raw materials
FLY ASH
ANHYDRITE
SAND
COKE
MILL-BLENDER
STORAGE SILO
FEED HOPPER
Tertiary air
DUST CYCLONE
ROTARY KILN
Secondary air
Fuel
Primary air
SCALE
CRUSHER
CLINKER STORAGE
Gypsum
CEMENT SILO
CEMENT MILL
Bagging, shipping
Dust
SO₂ gas
DRY ELECTROSTATIC PRECIPITATOR
COOLING AND SCRUBBING TOWERS
WET ELECTROSTATIC PRECIPITATOR
Air
DRYING TOWER
GAS BLOWER
SO₂ CONVERTER AND HEAT EXCHANGERS
SO₃ gas
Water
ABSORPTION TOWER
Waste gas
WASTE-GAS PRECIPITATOR
Waste gas to stack
Shipping
ACID STORAGE TANK

CHEMICAL ENGINEERING/NOVEMBER 4, 1963 113 114

R. RAMIREZ, 'GYPSUM FINDS NEW ROLE IN EASING SULFUR SHORTAGE,' CHEM. ENG., NO. 4, P. 112, (1968).

This section describes the tendency for disproportionation. The theoretical results obtained from partially estimated thermodynamic data are compared with experimental results for those sulfites for which experimental results were published.

Most of the experimental data has been contributed by Castellani and Co-workers. Their experiments were carried out in the following manner: the sulfites were heated at a rate of 10° C/minute and held for one hour at the final temperature. Next, they were cooled and analyzed. The samples were contained in a glass tube with a stream of nitrogen passing over them throughout the experiment.

Results:

1) $$4Li_2SO_3 \rightarrow 3Li_2SO_4 + Li_2S \qquad (34)$$

The tendency to disporportionate is shown for the whole temperature range of interest in Figure 29. The thermodynamic calculations are confirmed by experiment (GA-001). The disproportionation starts at about 650° C (see Figure 30 and Table 1). Thermal regeneration according to the scheme $Li_2SO_3 \rightarrow LiO + SO_2$ is, therefore, impossible at convenient temperatures.

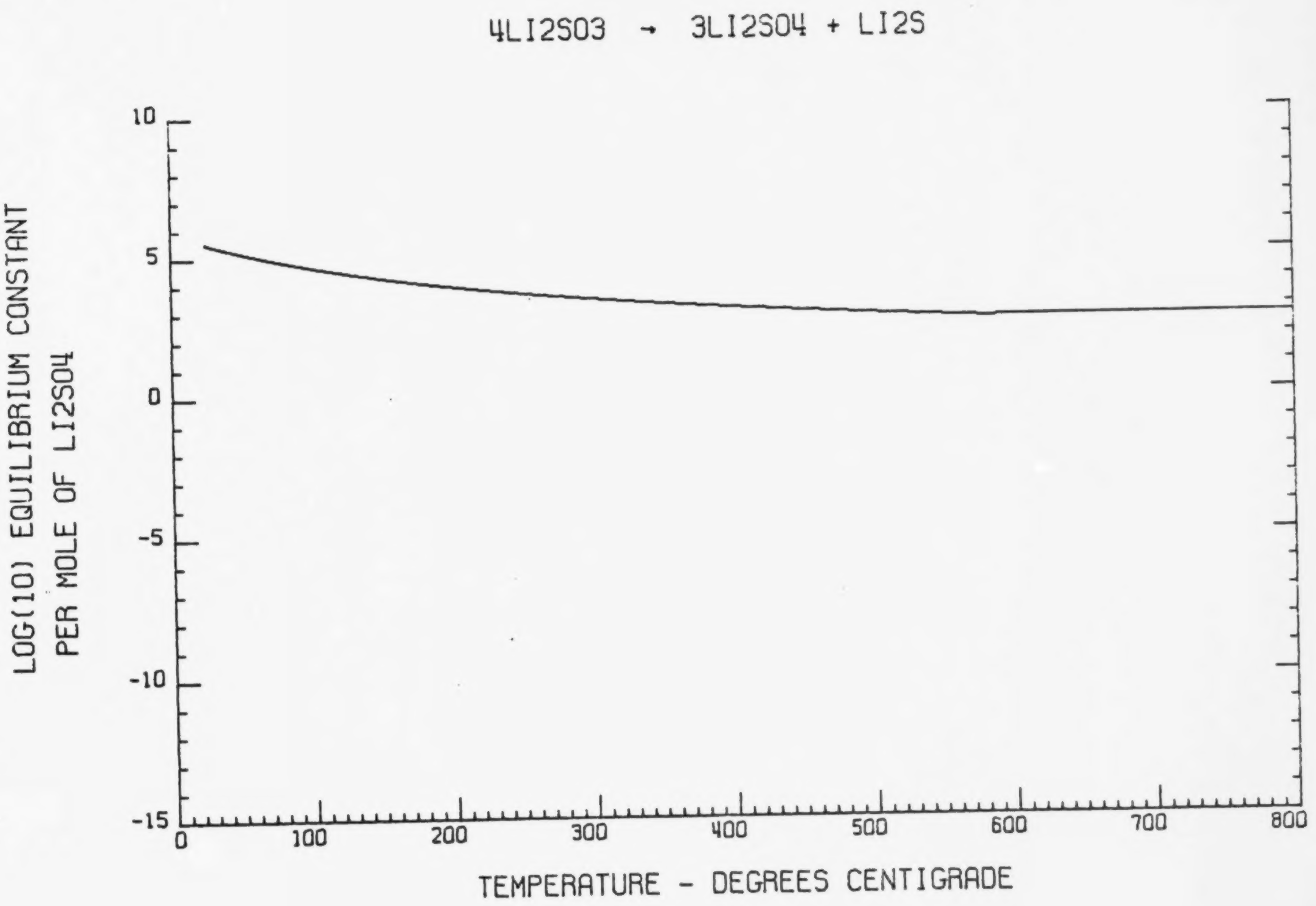

4LI2SO3 → 3LI2SO4 + LI2S
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF LI2SO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 29

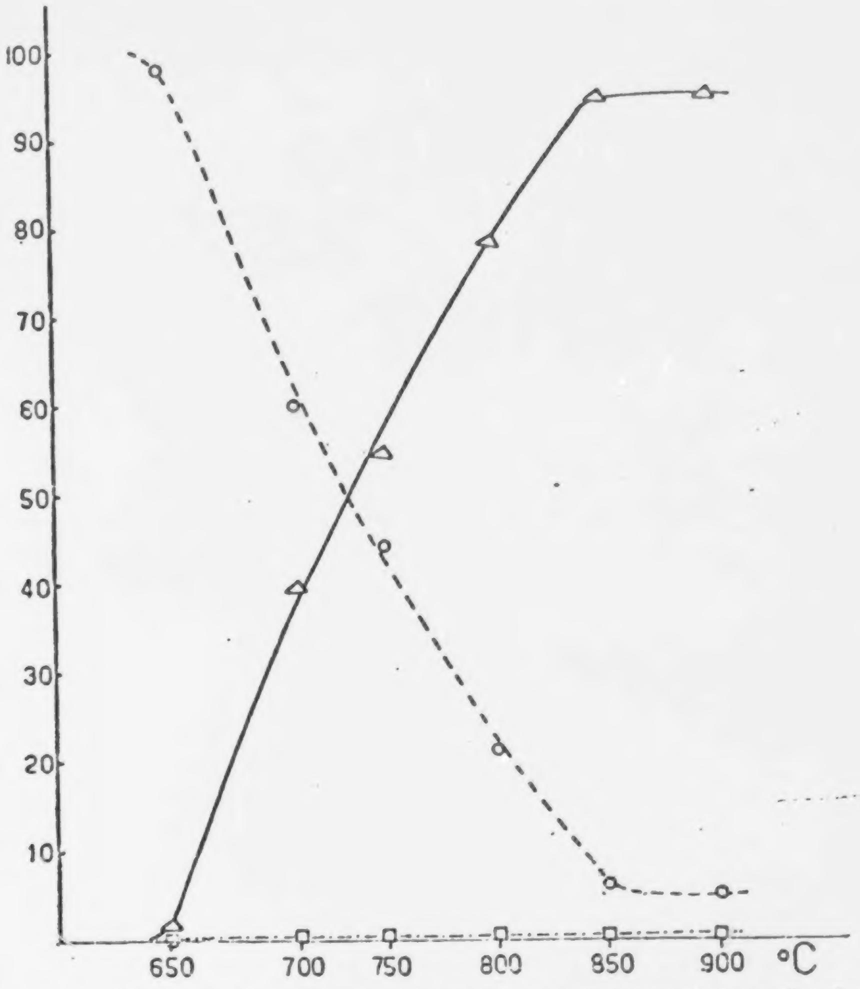


FIG. 2. - Grado di decomposizione di Li_2SO_3 in corrente di N_2 in funzione della temperatura

— -- — Li_2SO_3 residuo
--.--.— Li_2SO_3 dissociato
——— Li_2SO_4 dismutato

FIGURE 30 - The Disproportionation Behavior of Li_2SO_3 (GA-001)

residuo: unchanged

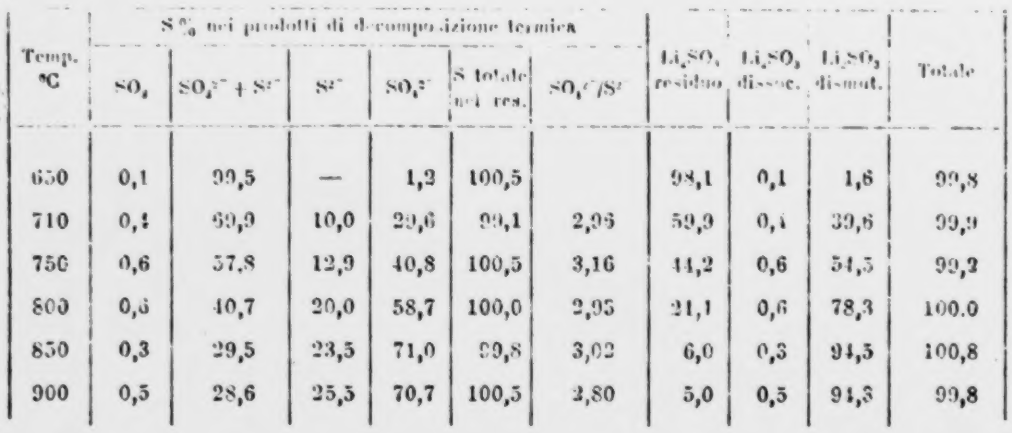
dissociato: decomposed according to the following equation:

$$Li_2SO_3 \rightarrow SO_2 + Li_2O$$

dismutato: disproportionation occurred according to the following equation:

$$4Li_2SO_3 \rightarrow 3Li_2SO_4 + Li_2S$$

E. RES. GARRINI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO,E AMMONIO,' GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).



Temp. °C	S % nei prodotti di decomposizione termica						Li$_2$SO$_3$ residuo	Li$_2$SO$_3$ dissoc.	Li$_2$SO$_3$ dismut.	Totale
	SO$_2$	SO$_3^{2-}$ + S^{2-}	S^{2-}	SO$_4^{2-}$	S totale nel res.	SO$_4^{2-}$/S^{2-}				
650	0,1	99,5	—	1,2	100,5		98,1	0,1	1,6	99,8
710	0,4	69,9	10,0	29,6	99,1	2,96	59,9	0,4	39,6	99,9
750	0,6	57,8	12,9	40,8	100,5	3,16	44,2	0,6	54,5	99,2
800	0,6	40,7	20,0	58,7	100,0	2,95	21,1	0,6	78,3	100.0
850	0,3	29,5	23,5	71,0	99,8	3,02	6,0	0,3	94,5	100,8
900	0,5	28,6	25,5	70,7	100,5	2,80	5,0	0,5	94,3	99,8

TABLE 1 - Summary of Analytical Results (GA-001). The molar ratio $SO_4^{=}/S^{=}$ is about three.

E. RES. GARRINI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO, E AMMONIO,' GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).

2) $4Na_2SO_3 \rightarrow 3NaSO_4 + Na_2S$ (35)

Na_2SO_3 also shows the thermodynamic tendency to disproportionate (see Figure 31). Experimental results were not found in the recent literature. The system was investigated earlier by F. Foerster and K. Kubel (FO-001). (See Table 2.)

Table 2 summarizes the Na_2SO_3 results. The tests made by Foerster and Kubel were run in a stream of nitrogen. The disproportionation began at about 600° C. Between 600 and 650° C sintering was observed. Melting occurred at 700° C. At 700° C nearly all sulfite was disproportionated. The specimens were heated to higher temperatures. Beginning at 800° C, SO_2 was detected in the exit nitrogen stream. At about 1200° C, Equation 33 was shifted to the right. Sodium sulfate and sulfide react with formation of Na_2O and SO_2. These results are given in graphical form in Figure 32.

3) $4K_2SO_3 \rightarrow 3K_2SO_4 + K_2S$ (35a)

The thermodynamic tendency to disproportionate exists in the whole temperature range investigated (see Figure 33). Here too, the results of the thermodynamic calculations are confirmed by the experiment. Figure 33a shows a graphical representation of the results given in Table 3. Disproportionation begins at 750° C. Here too, the ratio $SO_4^=/S^=$ is about three. At 1000° and 1050° C, however, the ratio is about five indicating a change in the overall reaction.

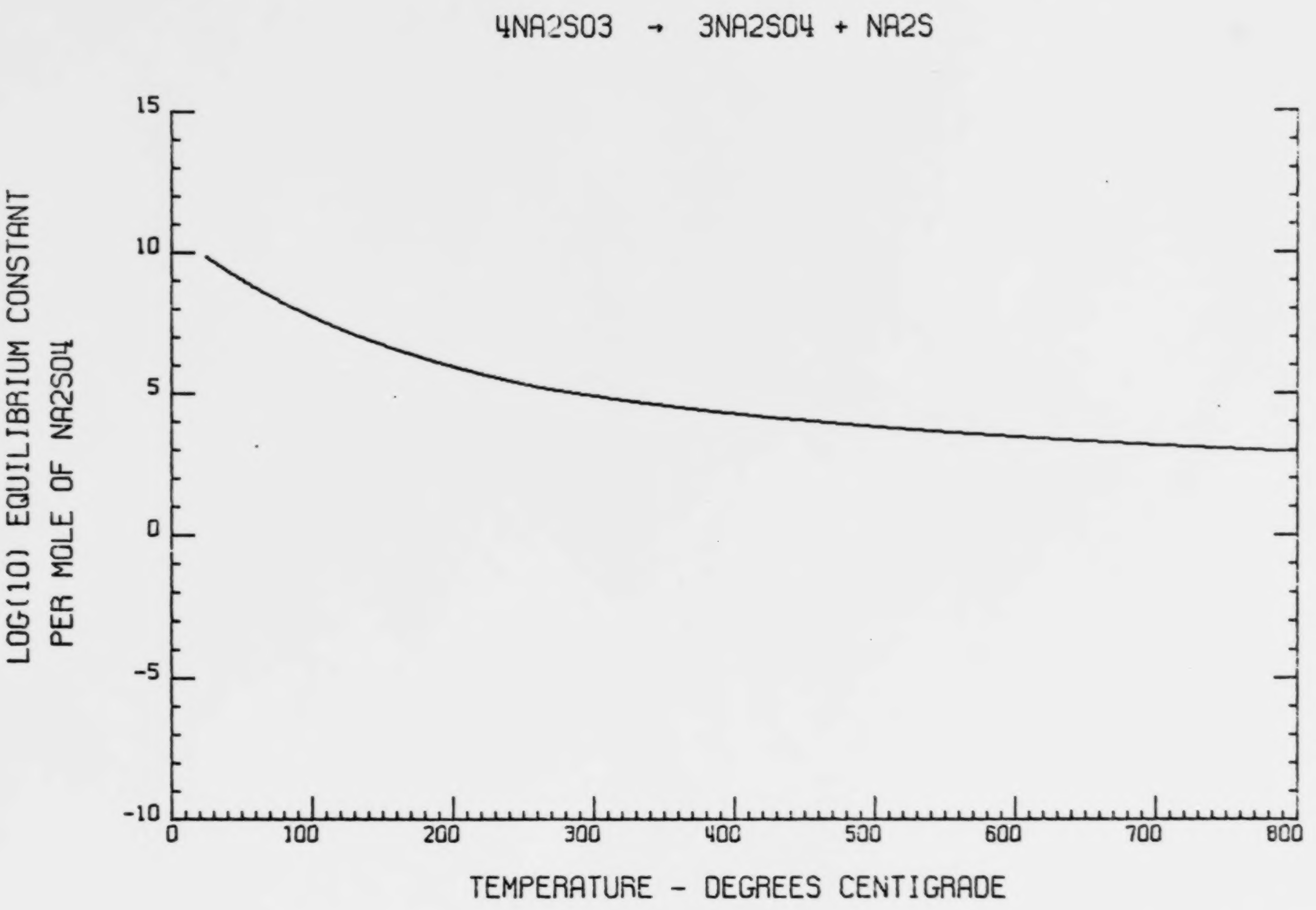

4NA2SO3 → 3NA2SO4 + NA2S
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF NA2SO4
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 31

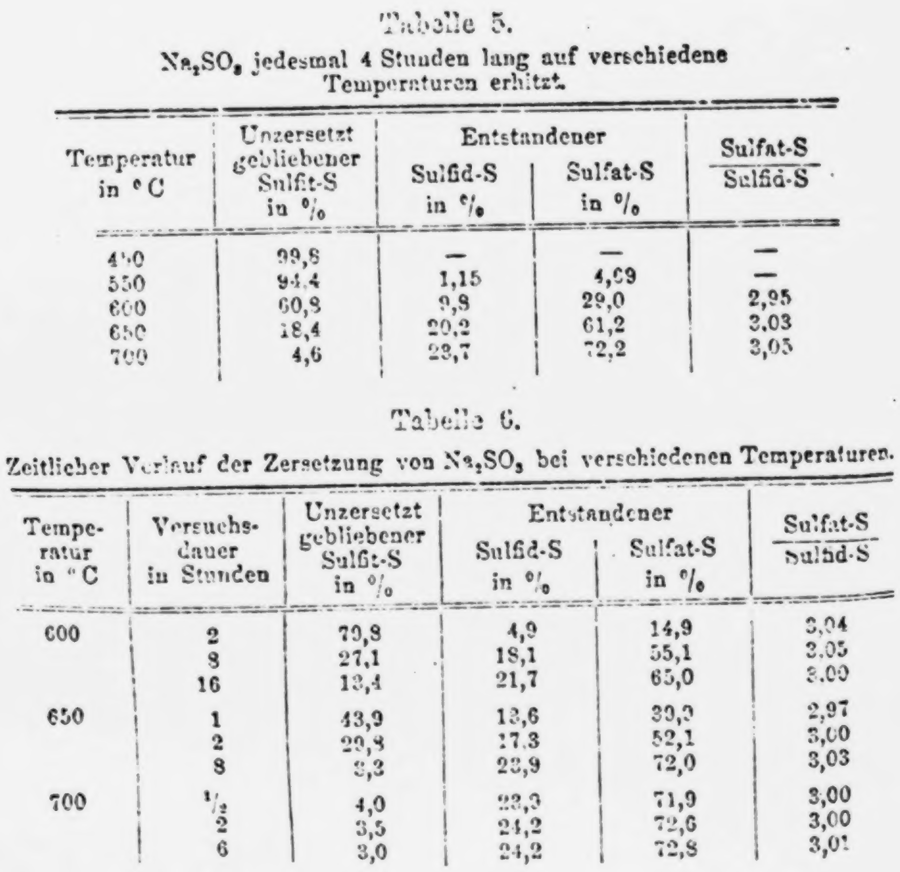


Tabelle 5.

Na_2SO_3 jedesmal 4 Stunden lang auf verschiedene Temperaturen erhitzt.

Temperatur in °C	Unzersetzt gebliebener Sulfit-S in %	Entstandener Sulfid-S in %	Entstandener Sulfat-S in %	$\frac{\text{Sulfat-S}}{\text{Sulfid-S}}$
450	99,8	—	—	—
550	94.4	1,15	4,09	—
600	60,8	9,8	29,0	2,95
650	18,4	20,2	61,2	3.03
700	4,6	23,7	72,2	3,05

Tabelle 6.

Zeitlicher Verlauf der Zersetzung von Na_2SO_3 bei verschiedenen Temperaturen.

Temperatur in °C	Versuchsdauer in Stunden	Unzersetzt gebliebener Sulfit-S in %	Entstandener Sulfid-S in %	Entstandener Sulfat-S in %	$\frac{\text{Sulfat-S}}{\text{Sulfid-S}}$
600	2	79,8	4,9	14,9	3,04
	8	27,1	18,1	55,1	3.05
	16	13,4	21,7	65,0	3.00
650	1	43,9	13,6	39,9	2,97
	2	29,8	17.3	52,1	3,00
	8	8,3	23,9	72,0	3,03
700	½	4,0	23,9	71,9	3,00
	2	3,5	24,2	72,6	3,00
	6	3,0	24,2	72,8	3,01

TABLE 2 - Decomposition Behavior of Na_2SO_3 (FO-001)

F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).

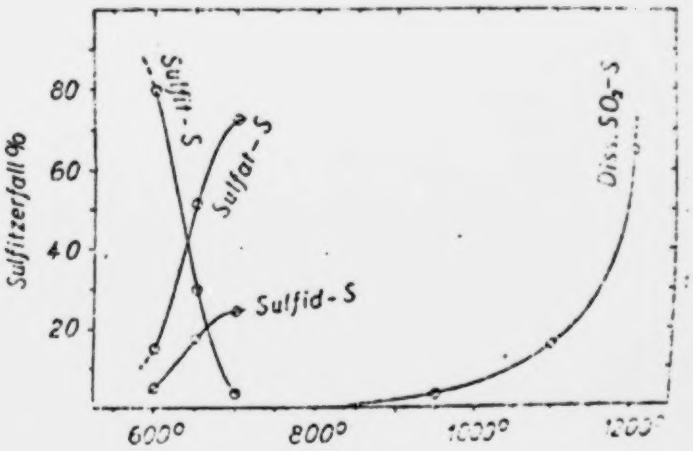


Fig. 5.

F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).

FIGURE 32 - Decomposition and Dissociation Behavior of Sodium Sulfite as a Function of Temperature

The specimen was held for two hours at the reaction temperature. Tests were performed in a stream of nitrogen (FO-001).

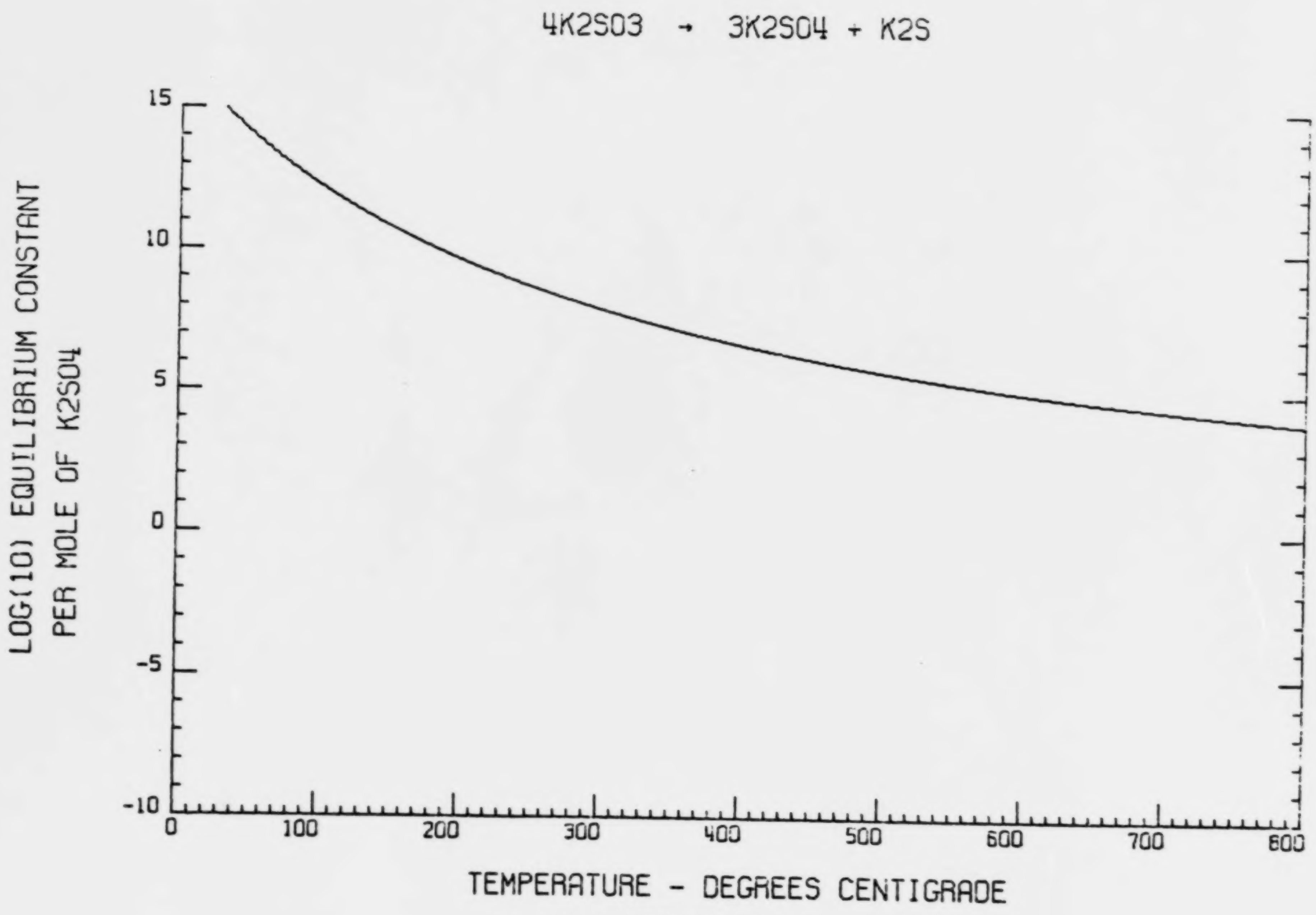

4K2SO3 → 3K2SO4 + K2S
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF K2SO4
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 33

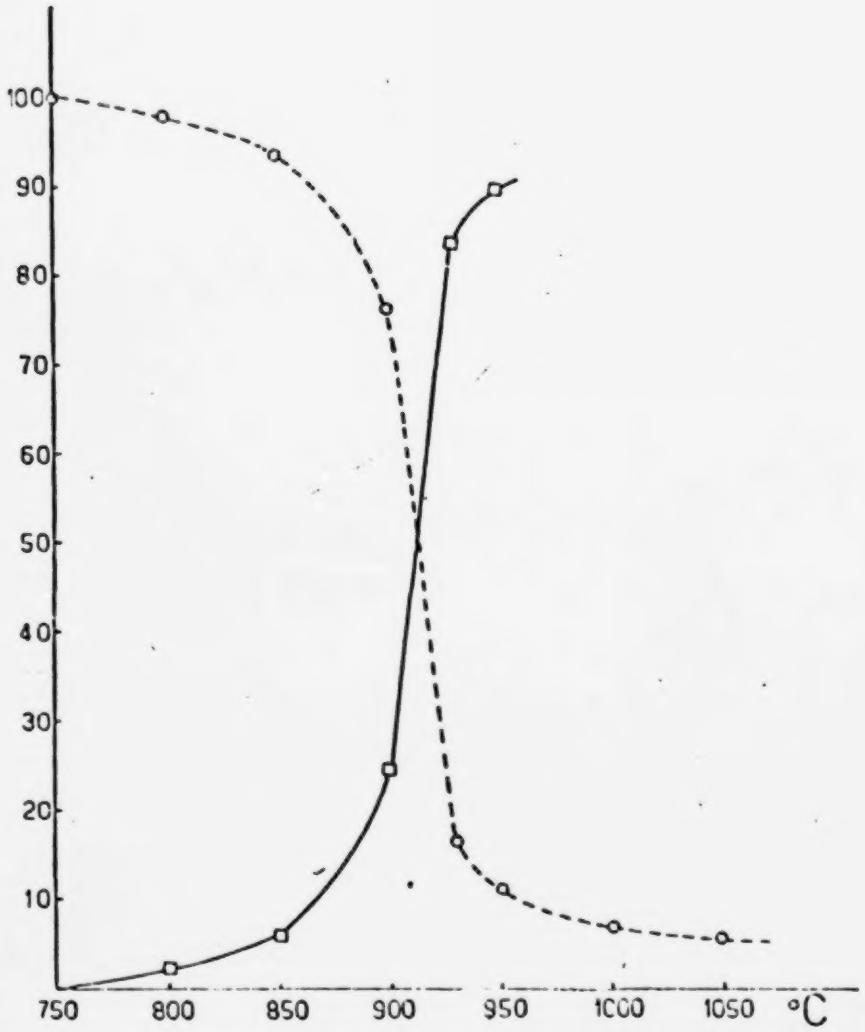
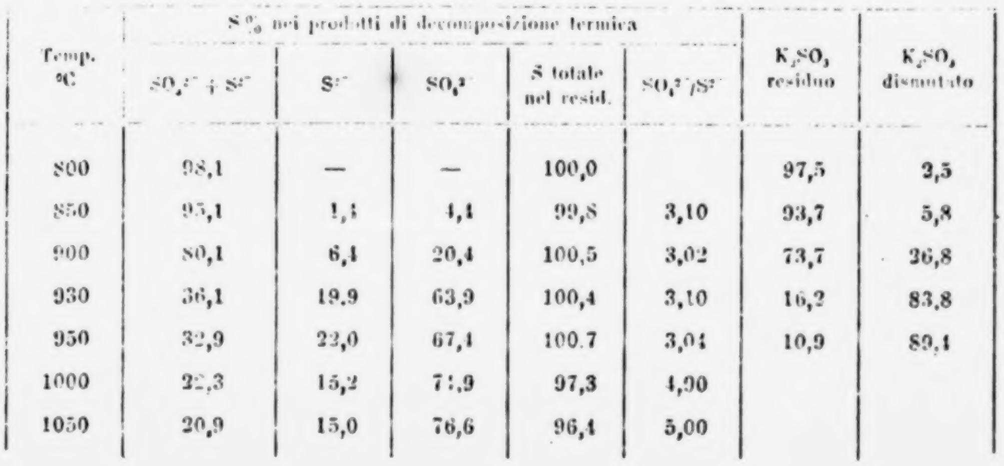


Fig. 1. - Grado di decomposizione di K_2SO_3 in corrente di N_2 in funzione della temperatura

FIGURE 33a - Thermal Decomposition of K_2SO_3 in Nitrogen (GA-001)

E. RES. GARRINI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO,E AMMONIO,' GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).



Temp. °C	S % nei prodotti di decomposizione termica					K_2SO_3 residuo	K_2SO_3 dismutato
	$SO_3^{2-} + S^{2-}$	S^{2-}	SO_4^{2-}	S totale nel resid.	SO_4^{2-}/S^{2-}		
800	98,1	—	—	100,0		97,5	2,5
850	95,1	1,4	4,4	99,8	3,10	93,7	5,8
900	80,1	6,4	20,4	100,5	3,02	73,7	26,8
930	36,1	19.9	63,9	100,4	3,10	16,2	83.8
950	32,9	22,0	67,4	100.7	3,04	10,9	89,1
1000	22,3	15,2	74,9	97,3	4,90		
1050	20,9	15,0	76,6	96,4	5,00		

TABLE 3 - Summary of Analytical Results for Disproportionation of Potassium Sulfite (GA-001)

E. RES. GARBINI, C. CASTELLANI BISI, "DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO, E AMMONIO," GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).

4) Rubidium and Cesium Sulfite

Thermodynamic calculations could not be made for these compounds because of the lack of thermodynamic data.

No experimental results were published. From the position in the periodic table and from the properties of lithium, sodium, and potassium sulfite as well as from the stability of the sulfates, one can predict that sorption is thermodynamically possible and that kinetically the sulfite will begin to disproportionate at temperatures $\approx 750°C$. At temperatures $< 750°C$, a thermal regeneration will be thermodynamically impossible.

5) $$4BeSO_3 \rightarrow 3BeSO_4 + BeS \qquad (36)$$

No literature was found describing the thermal behavior of $BeSO_3$. According to Figure 34, $BeSO_3$ shows no tendency to disproportionate. Beryllium oxide is apparently of no use in SO_2 adsorption if the product is assumed to be the sulfite, since the upper temperature limit of stability is only 150° C (see Figure 5).

6) $$4MgSO_3 \rightarrow 3MgSO_4 + MgS \qquad (37)$$

The disproportionation is thermodynamically favored in the entire temperature range (see Figure 35).

With a decomposition temperature of about 350° C (see Figure 6), however, one can expect that the decomposition reaction is important. The decomposition behavior was investigated by Ketov and Pechkovskii (KE-006). The following experimental technique was used.

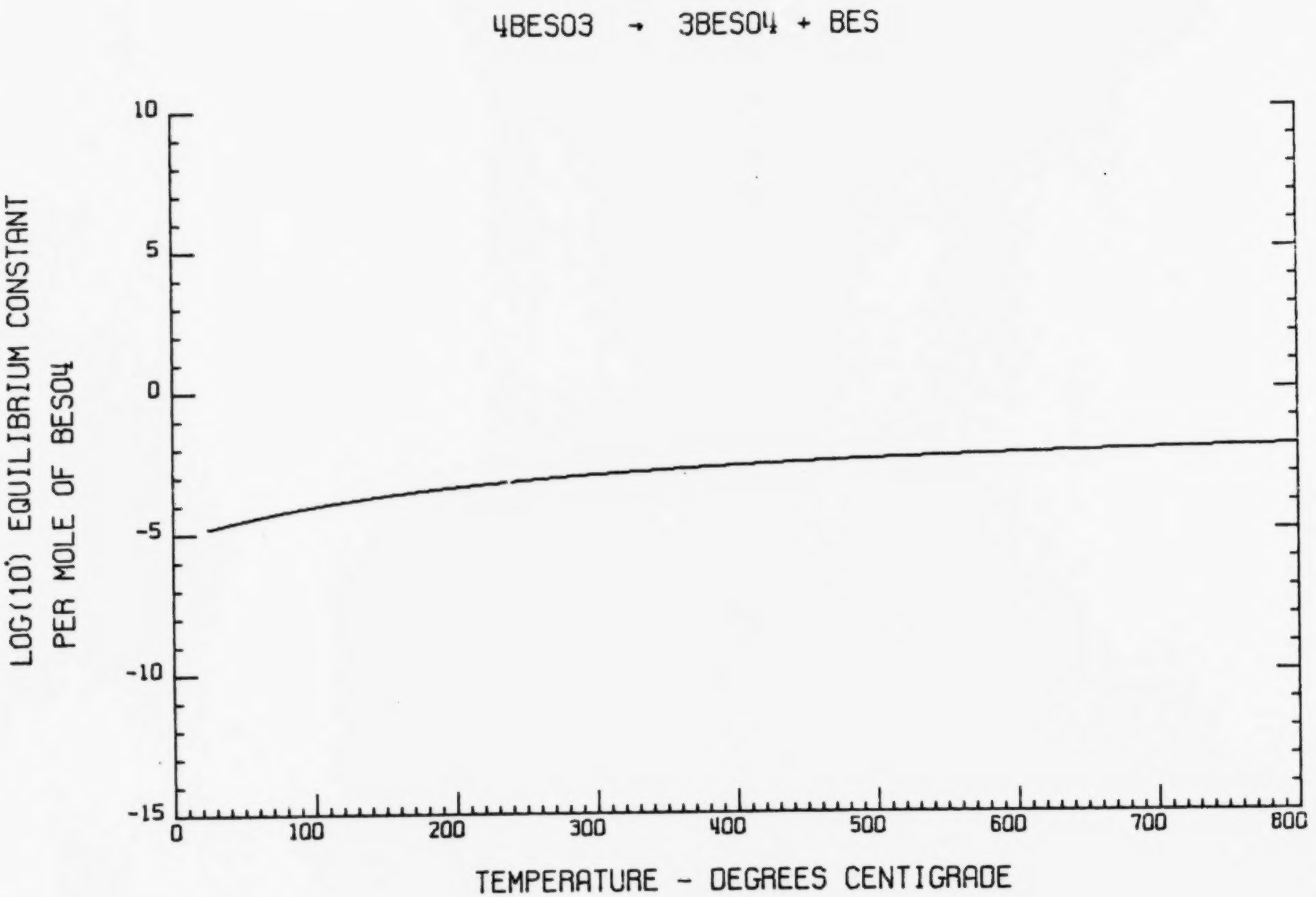

4BESO3 → 3BESO4 + BES
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF BESO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 34

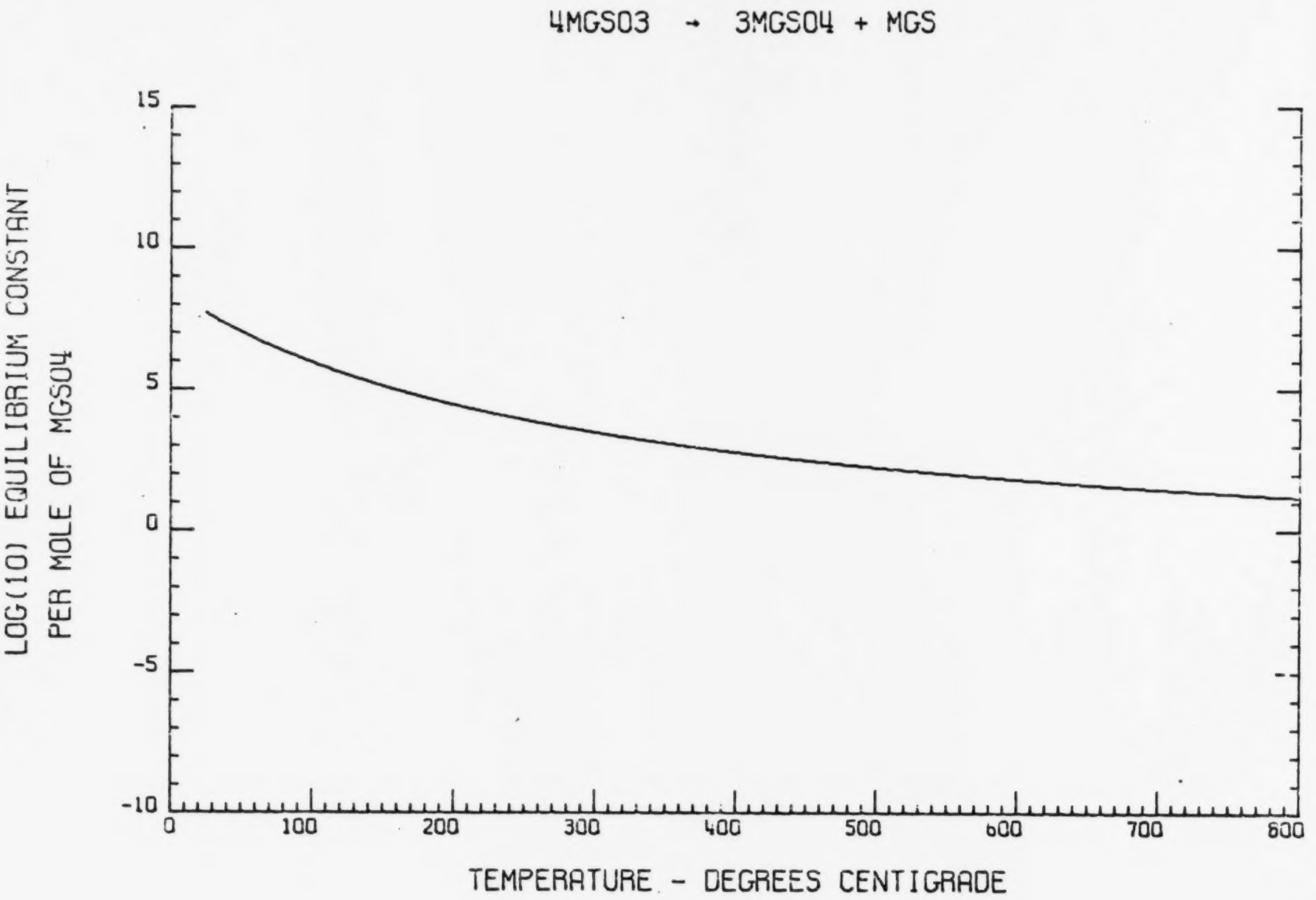

4MGSO3 → 3MGSO4 + MGS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF MGSO4
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 35

"The magnesium sulphite (0.5 g in all experiments) or a mixture of it with various additions, amounting to 10% of the initial $MgSO_3$, was placed in a porcelain boat and ignited in a laboratory tube furnace in a current of gas at 300° to 600°. After the experiment the boat with the residue was carefully moved to a cold portion of the furnace, where it was cooled in a current of the same gas in which the magnesium sulphite has been decomposed···. The gas flow was 3.0 l/h in all cases and the experiments lasted for 15 min.

The gaseous and solid products from the thermal decomposition of the magnesium sulphite were analysed, the former for the sulphur dioxide, hydrogen sulphide and sulphur, and the latter for magnesium sulphite, thiosulphate, sulphate and sulphur." (KE-006 p.118)

Tables 4 through 7 and Figure 36 summarize the results.

The authors proposed the following reactions:

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (38)$$

$$2\ MgSO_3 + SO_2 \rightarrow 2MgSO_4 + \tfrac{1}{2}S_2 \qquad (39)$$

The validity of the second equation was proven by heating magnesium sulfite in a 100% SO_2 atmosphere at 400° C. Dissociation did not occur. The reaction products were $MgSO_4$, MgS_2O_3, and S_2. The thiosulfate is formed by the reaction shown in Equation 40.

$$MgSO_3 + \tfrac{1}{2}S_2 \rightarrow MgS_2O_3 \qquad (40)$$

TABLE 1. Effect of temperature on the degree of thermal decomposition of magnesium sulphite in a current of nitrogen.

Temp., °C	% conversion of S of $MgSO_3$				
	SO_2	MgS_2O_3	S	$MgSO_4$	Total
300	0.7	2.1	2.0	5.7	10.5
350	2.1	3.6	2.6	8.8	17.1
400	5.7	4.8	3.1	10.8	24.4
450	16.3	5.3	3.8	12.9	38.3
500	36.8	4.5	5.2	14.9	61.4
550	68.5	0.0	8.4	17.5	94.4
600	88.2	0.0	3.9	7.8	99.9

TABLE 4

A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

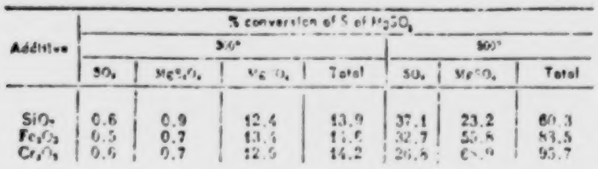
TABLE 2. Dependence of the degree of thermal decomposition of magnesium sulphite on the temperature and the concentration of oxygen in the gas passed over the sulphite.

Conc. of O_2, %	% conversion of S of $MgSO_3$												
	300°				400°			500°			600°		
	SO_2	MgS_2O_3	$MgSO_4$	Total	SO_2	$MgSO_4$	Total	SO_2	$MgSO_4$	Total	SO_2	$MgSO_4$	Total
21	0.6	0.8	12.9	14.3	4.7	25.8	30.5	37.9	24.7	62.6	81.7	17.7	99.4
100	0.4	0.0	17.1	17.5	3.6	31.3	34.9	28.4	36.5	64.9	71.4	27.6	99.0

TABLE 5

A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

TABLE 3. Dependence of the degree of thermal decomposition of magnesium sulphite on the temperature and the nature of additive in a current of air. 10% of additive present.

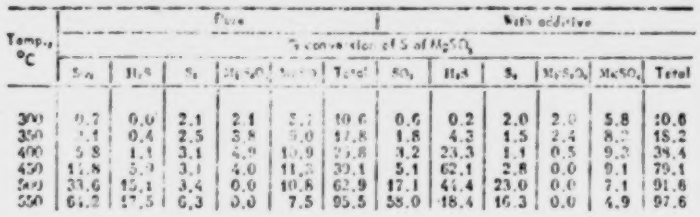


Additive	% conversion of S of $MgSO_3$						
	500°				900°		
	SO_2	MgS_2O_3	$MgSO_4$	Total	SO_2	$MgSO_4$	Total
SiO_2	0.6	0.9	12.4	13.9	37.1	23.2	60.3
Fe_2O_3	0.5	0.7	13.4	14.6	32.7	55.8	83.5
Cr_2O_3	0.6	0.7	12.9	14.2	26.8	68.9	95.7

TABLE 6

A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

TABLE 4. Temperature dependence of thermal decomposition of magnesium sulphite, pure and with addition of 10% bauxite, in a current of hydrogen.



Temp., °C	Pure						With additive					
	% conversion of S of $MgSO_3$											
	SO_2	H_2S	S_2	MgS_2O_3	$MgSO_4$	Total	SO_2	H_2S	S_2	MgS_2O_3	$MgSO_4$	Total
300	0.7	0.0	2.1	2.1	5.7	10.6	0.6	0.2	2.0	2.0	5.8	10.6
350	2.1	0.4	2.5	3.8	9.0	17.8	1.8	4.3	1.5	2.4	8.2	18.2
400	5.8	1.1	3.1	4.9	10.9	25.8	3.2	23.3	1.1	0.5	9.2	38.4
450	14.8	5.9	3.1	4.0	11.3	39.1	5.1	62.1	2.8	0.0	9.1	79.1
500	33.6	15.1	3.4	0.0	10.8	62.9	17.1	44.4	23.0	0.0	7.1	91.6
550	64.2	17.5	6.3	0.0	7.5	95.5	58.0	18.4	16.3	0.0	4.9	97.6

TABLE 7

A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

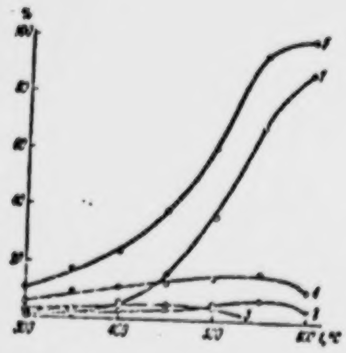


Fig. 1. Dependence of the degree of decomposition of magnesium sulphite on temperature in a current of nitrogen. Percentage conversion of the sulphur of $MgSO_3$ into:

1) sulphur dioxide; 2) elemental sulphur; 3) magnesium sulphate; 5) total.

FIGURE 36

A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

In the presence of air, $MgSO_3$ is oxidized to sulfate as shown in Equation 41.

$$MgSO_3 + \frac{1}{2}O_2 \rightarrow MgSO_4 \qquad (41)$$

The decomposition in hydrogen is nearly the same as that in nitrogen. Sulfur is partly reduced to H_2S.

7) $$4CaSO_3 \rightarrow 3CaSO_4 + CaS \qquad (42)$$

The thermodynamic calculations show a tendency to disproportionate in the whole temperature range (see Figure 37). The decomposition and disproportionation behavior of calcium sulfite was investigated experimentally by Foerster and Kubel (FO-001). The experiments were done with a stream of nitrogen passing over the specimen. The specimen was dehydrated at 380-390° C, heated to the final temperature and held there for about an hour.

Tables 8 and 9 summarize the results as a function of temperature up to 800° C. Sulfide and sulfate are formed in the molar ratio 1:3. At temperatures higher than 800° C $CaSO_3$ shows a behavior similar to Na_2SO_3 (see Figure 32). Here too Equation 33 is shifted to the right (see Figure 38).

8) $$4SrSO_3 \rightarrow 3SrSO_4 + SrS \qquad (43)$$

The results of the thermodynamic calculations are shown in Figure 39. $SrSO_3$ shows the tendency to disproportionate between 25° and 800° C. The experimental results of Cola and Castellani Bisi (CO-004) are given in Table 10 and Figure 40.

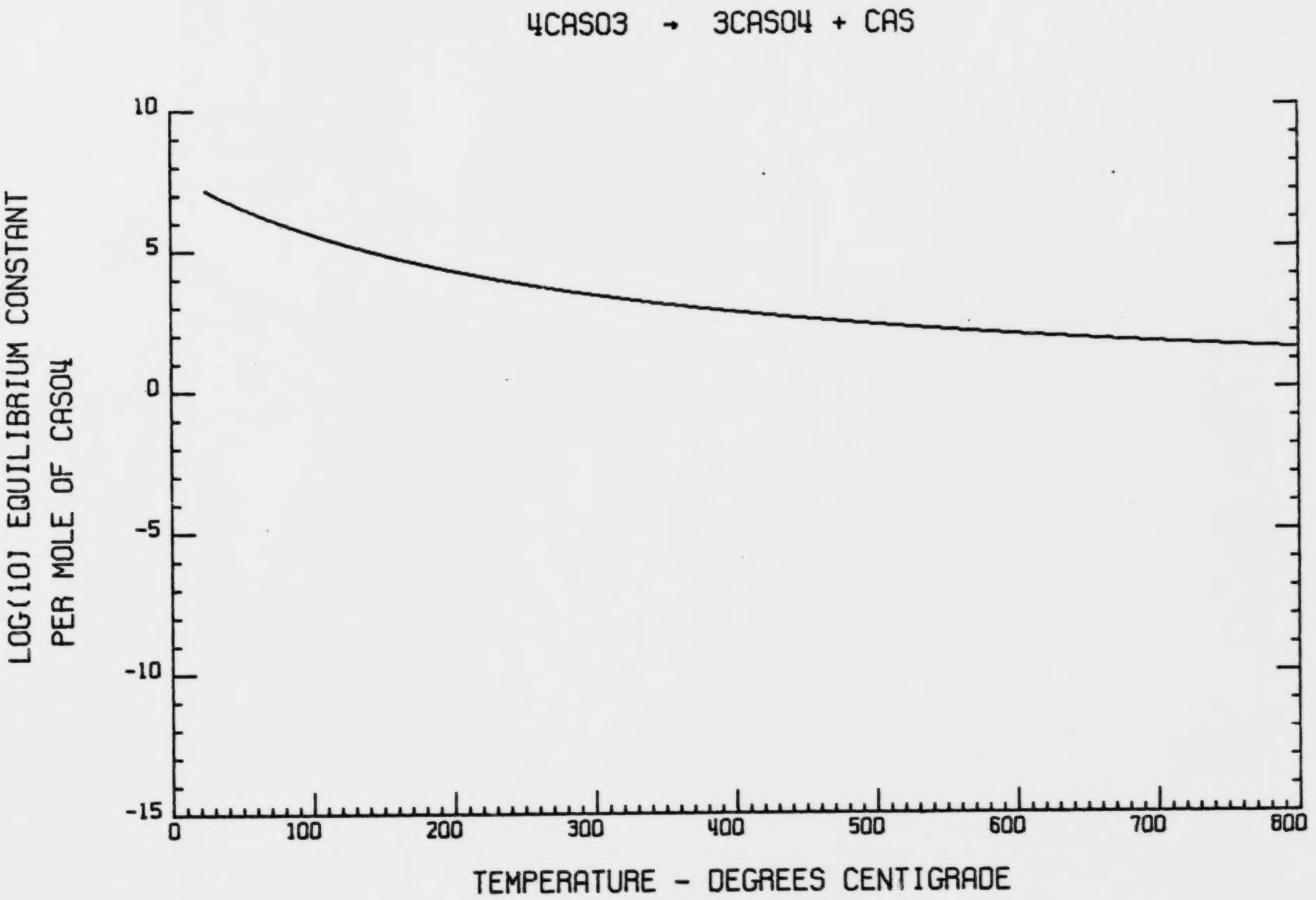
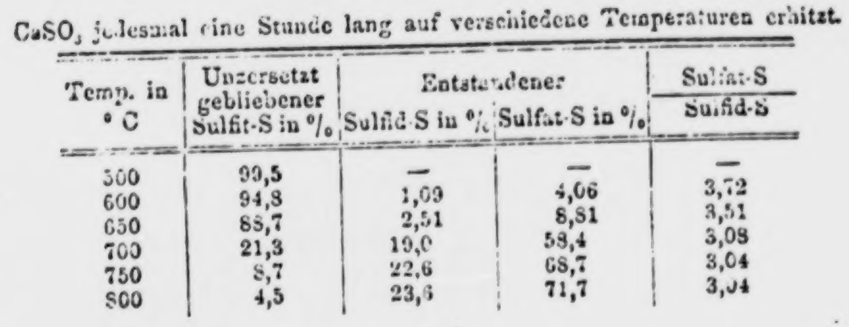

4CASO3 → 3CASO4 + CAS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF CASO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 37



$CaSO_3$ jedesmal eine Stunde lang auf verschiedene Temperaturen erhitzt.

Temp. in °C	Unzersetzt gebliebener Sulfit-S in %	Entstandener		$\frac{\text{Sulfat-S}}{\text{Sulfid-S}}$
		Sulfid-S in %	Sulfat-S in %	
500	99,5	—	—	—
600	94,8	1,09	4,06	3,72
650	88,7	2,51	8,81	3,51
700	21,3	19,0	58,4	3,08
750	8,7	22,6	68,7	3,04
800	4,5	23,6	71,7	3,04

F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).

TABLE 8 - Decomposition and Disproportionation Behavior of $CaSO_3$ as a Function of Temperature.

Heating time one hour (FO-001).

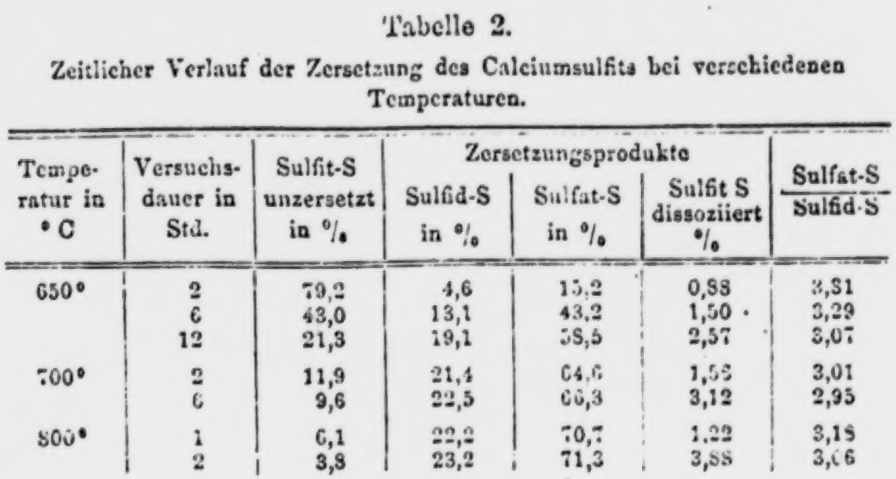


Tabelle 2.

Zeitlicher Verlauf der Zersetzung des Calciumsulfits bei verschiedenen Temperaturen.

Temperatur in °C	Versuchsdauer in Std.	Sulfit-S unzersetzt in %	Zersetzungsprodukte			$\frac{\text{Sulfat-S}}{\text{Sulfid-S}}$
			Sulfid-S in %	Sulfat-S in %	Sulfit S dissoziiert %	
650°	2	79,2	4,6	15,2	0,88	3,31
	6	43,0	13,1	43,2	1,50	3,29
	12	21,3	19,1	58,5	2,57	3,07
700°	2	11,9	21,4	64,6	1,56	3,01
	6	9,6	22,5	66,3	3,12	2,95
800°	1	6,1	22,2	70,7	1,22	3,18
	2	3,8	23,2	71,3	3,88	3,06

TABLE 9 - Decomposition of $CaSO_3$ as a Function of Temperature and Time (FO-001).

F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).

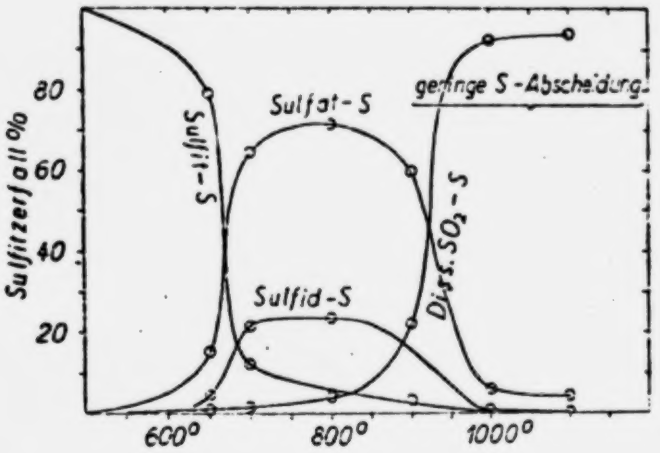


FIGURE 38 - Disproportionation and Decomposition Behavior of $CaSO_3$ Between 500° C and 1100° C (FO-001).

F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).

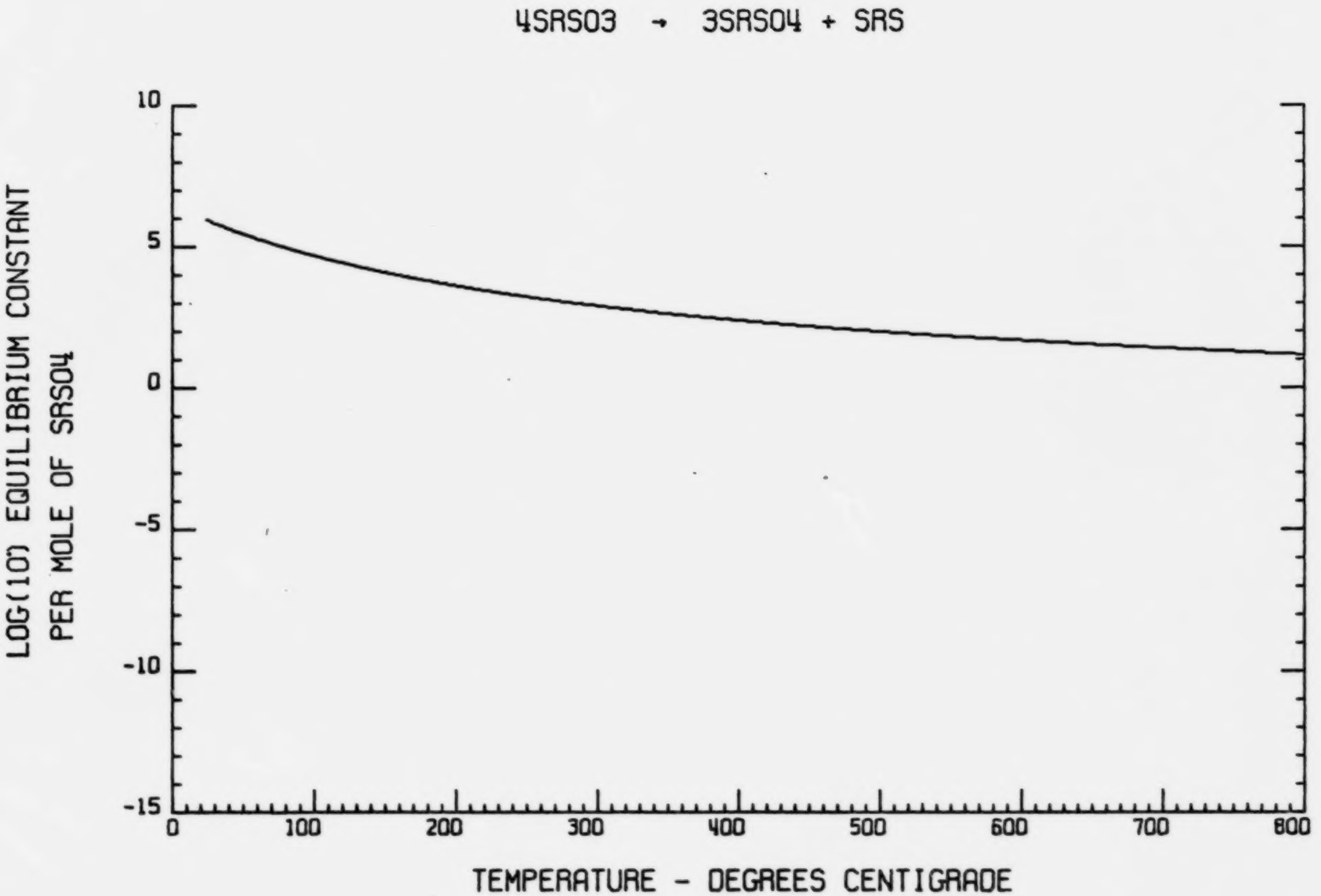

4SRSO3 → 3SRSO4 + SRS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SRSO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 39

ESPERIENZE DI RISCALDAMENTO DI $SrSO_3$ IN CORRENTE DI AZOTO

Temp. °C	$SrSO_3$ residuo	$SrSO_4$ calcolato	$SrSO_4$ trovato	$SrSO_3$ dissociato	$SrSO_3$ dismutato	$SrSO_3$ totale
420	99.5	—	—	—	—	—
478	97.8	1.8	2,0	—	2,1	100,2
525	90,0	8,2	9.0	—	10,9	100,9
570	83,5	13,6	13.7	—	16.7	100.2
620	71.5	23,1	23.1	0.3	28.1	99.9
680	19.2	66,1	65.1	0.1	79.6	99.2
740	3,6	79,2	80.9	0.5	98,5	102,6
815	—	82,2	82.8	0.7	100,8	101.5

TABLE 10 - Analytical Results of $SrSO_3$ Decomposition (CO-004)

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

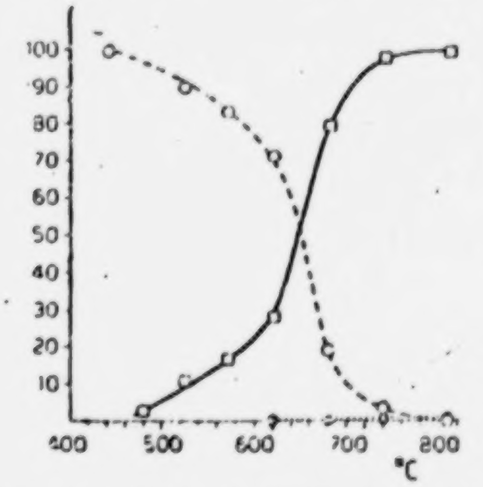


FIG. 3. - Grado di decomposizione di $SrSO_3$ in corrente di azoto in funzione della temperatura

- - - - - $SrSO_3$ residuo
——— $SrSO_3$ dismutato
······· $SrSO_3$ dissociato

FIGURE 40

Graphical representation of the results shown in Table 10 (CO-004).

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

$SrSO_3$ begins to disproportionate at about 450° C. The disproportionation reaction alone occurs over practically the whole temperature range investigated. Theoretical decomposition temperature is > 800° C (see Figure 8).

9) $4BaSO_3 \rightarrow 3BaSO_4 + BaS$ (44)

The results of the thermodynamic calculations are represented in Figure 41. $BaSO_3$ also has the tendency to disproportionate in the whole temperature range of interest.

The experimental results published by Cola and Castellani Bisi (CO-004) are summarized in Table 11 and Figure 42. The disproportionation begins at about 400° C. Here too, the disproportionation alone occurs over practically the entire temperature range investigated. Theoretical decomposition temperature is > 800° C.

10) Scandium Sulfite
11) Yttrium Sulfite
12) Lanthanum Sulfite

Theoretical calculations cannot be made for the above sulfites since some data are lacking. Fortunately there are experimental results from Castellani Bisi and Aldo Clerici (CL-001). The results are given in Tables 12, 13, and 14.

Figure 43 shows the results in graphical form. The rate of disproportionation reaction becomes comparible to the decomposition reaction. This is also true for samarium and seems to be a characteristic for the lanthanides.

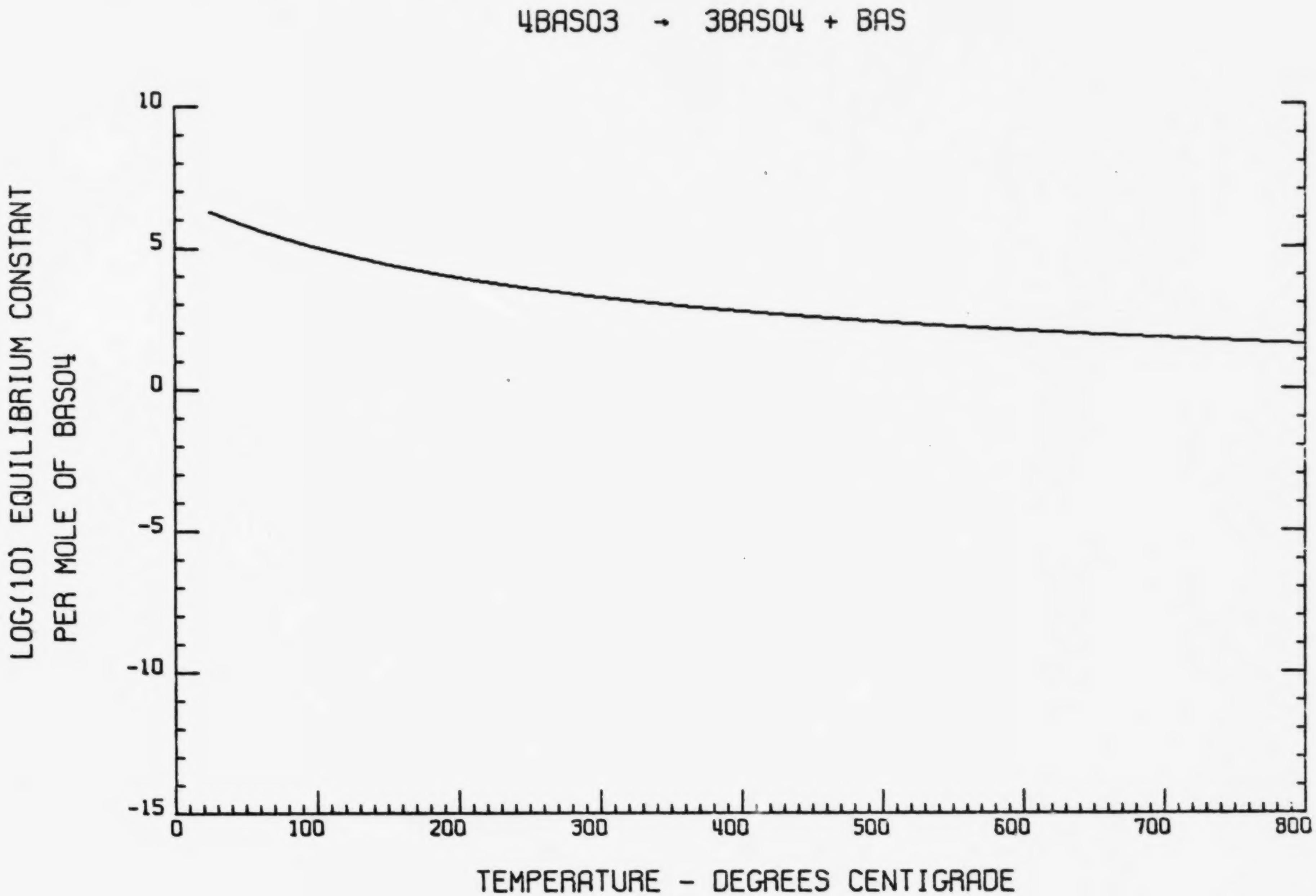

4BASO3 → 3BASO4 + BAS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF BASO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 41

Esperienze di riscaldamento di $BaSO_3$ in corrente di azoto

Temp. °C	$BaSO_3$ residuo	$BaSO_4$ calcolato	$BaSO_4$ trovato	$BaSO_3$ dissociato	$BaSO_3$ dismutato	$BaSO_3$ totale
400	99.0	—				
460	96.0	3.2	2.1	—	2,6	98.6
520	92.6	6.0	4.0	—	5,0	97.6
524	91.5	4.4	3,6	—	4,5	99.0
570	76.9	18.6	16.7	0,2	20,7	97.6
574	84.0	12.9	12.7	0.2	15,8	100.0
606	60,0	32.2	30,0	0.3	37.3	97.6
648	29.4	56.8	54.4	0,4	67.6	97.4
650	29.0	57.2	57.0	0,4	70,8	100.2
685	16.6	67.2	66,3	0.5	82.3	99,4
688	20.0	61,4	63,5	0,5	78,9	99,1
713	11.5	71.3	71.1	0,6	88,3	100.4
745	6.4	75,4	76.0	0,6	91.4	101.4
746	9,8	72.6	74,0	0,6	91.9	101,7
802	—	80.5	84.3	0.8	—	—
820	—	80.5	83,6	0,8	—	—

TABLE 11 - Experimental Results for $BaSO_4$ Disproportionation

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

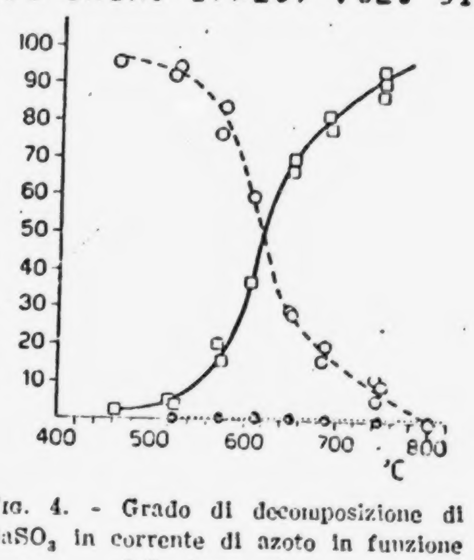


FIG. 4. - Grado di decomposizione di $BaSO_3$ in corrente di azoto in funzione della temperatura

- - - - - $BaSO_3$ residuo
——— $BaSO_3$ dismutato
······· $BaSO_3$ dissociato

FIGURE 42 - Graphical Representation of the Results in Table 11 (CO-004)

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

ESPERIENZE DI RISCALDAMENTO DI $Sc_2(SO_3)_3$ IN CORRENTE DI N_2

Temp. °C	S % nei prodotti di decomposizione termica						Totale
	S iodometr. titolabile nei gas	S fissato da Ag	S iodometr. titolabile nel residuo	$S^{=}$	SO_4^{2-}	S totale nel residuo	
300	0,6	0,04	98,1	—	1,8		100,6
350	9,7	0,2	84,1	--	6,8		100,8
400	21,3	0,2	64,6	tracce	9,5	75,6	98,3
450	53,4	2,0	30,7	—	9,0	45,1	100,4
500	62,4	3,8	16,4	—	14,5	31,6	99,9
550	62,3	3,4	14,3	—	14,7	33,6	99,2

TABLE 12 - Thermal Decomposition of $Sc_2(SO_3)_3$ (CL-001)

A. CLERICI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI SCANDIO, ITTRIO, LANTANIO, NEODIMIO, SAMARIO,' GAZZ. CHIM. ITAL., VOL. 93, PP. 1444-54 (1963).

Temp. °C	S % nei prodotti di decomposizione termica						Totale
	S iodometr. titolabile nei gas	S fissato da Ag	S iodometr. titolabile nel residuo	$S^{=}$	SO_4^{2-}	S totale nel residuo	
500	1,8	—	94,7	—	4,4	98,8	100,9
550	3,9	—	93,9	—	4,8	98,9	101,6
600	5,9	—	85,6	tracce	6,6	95,2	101,3
650	20,4	tracce	69,9	tracce	7,6	82,1	103,9
700	28,6	0,7	60,2	—	11,4	69,2	98,6
750	36,2	4,0	40,6	—	15,9	56,8	97,0
800	70,4	5,4	1,5	—	23,0	23,4	100,4

TABLE 13 - Thermal Decomposition of $Y_2(SO_3)_3$ (CL-001)

ESPERIENZE DI RISCALDAMENTO DI $La_2(SO_3)_3$ IN CORRENTE DI N_2

Temp. °C	S % nei prodotti di decomposizione termica					Totale
	S iodometr. titolabile nei gas	S fissato da Ag	S iodometr. titolabile nel residuo	SO_4^{2-}	S totale nel residuo	
400	0,4	--	90,3	11,6	101,6	102,0
450	0,5	—	88,1	11,0	100,3	100,7
500	1,3	--	83,5	17,6	100,7	102,0
550	2,2	--	55,3	39,0	99,5	101,7
600	3,2	—	46,9	40,9	98,2	101,3
650	16,0	6,2	21,8	52,0	74,5	96,7
700	32,9	19,3	3,0	46,9	47,2	99,0

TABLE 14 - Thermal Decomposition of $La_2(SO_3)_3$ (CL-001)

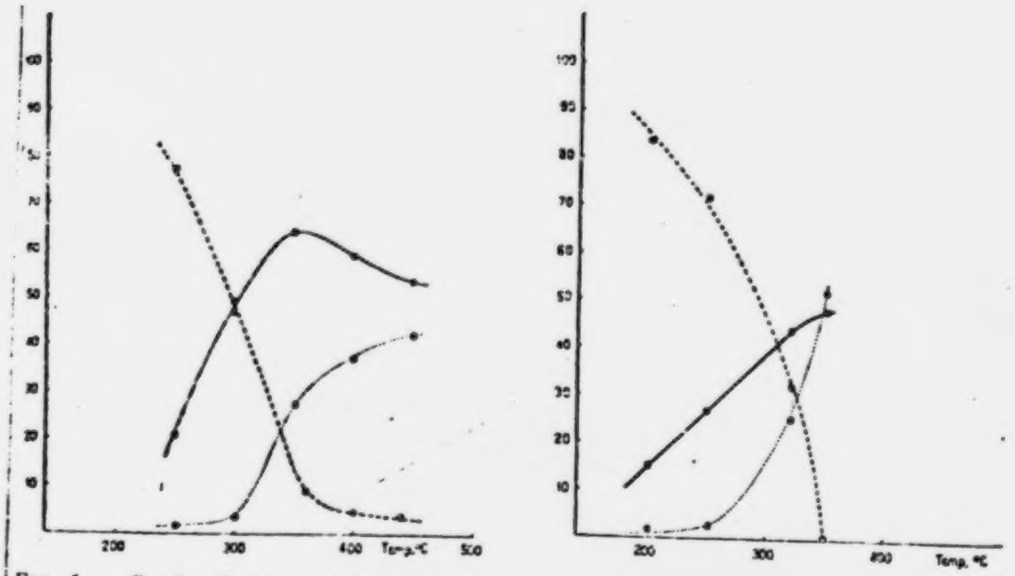


FIG. 1. - Grado di decomposizione di $La_2(SO_3)_3$ in corrente di N_2
- - - - $La_2(SO_3)_3$ residuo
····· $La_2(SO_3)_3$ dissociato
—— $La_2(SO_3)_3$ dismutato

FIG. 2. - Grado di decomposizione di $Sm_2(SO_3)_3$ in corrente di N_2
- - - - $Sm_2(SO_3)_3$ residuo
····· $Sm_2(SO_3)_3$ dissociato
—— $Sm_2(SO_3)_3$ dismutato

FIGURE 43 - Decomposition Behavior of Lanthanum and Samarium Sulfite

A. CLERICI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI SCANDIO, ITTRIO, LANTANIO, NEODIMIO, SAMARIO,' GAZZ. CHIM. ITAL., VOL. 93, PP. 1444-54 (1963).

These sulfites showed the peculiarity that sulfur in the form of sulfide was not found in the residue. The disproportionation reaction, Equation 45,

$$4Sc_2(SO_3)_3 \rightarrow 3Sc_2SO_4)_3 + Sc_2S_3 \qquad (45)$$

and the decomposition reaction, Equation 46,

$$Sc_2(SO_3)_3 \rightarrow Sc_2O_3 + 3SO_2 \qquad (46)$$

are followed by side reactions such as Equation 47.

$$Sc_2S_3 + 6SO_2 \rightarrow Sc_2(SO_4)_3 + 3S_2 \qquad (47)$$

Another side reaction which leads to the formation of sulfur is shown in Equations 48 and 49.

$$4Sc_2(SO_3)_3 \rightarrow Sc_2(S_2O_3)_3 + 2Sc_2(SO_4)_3 + Sc_2O_3 \qquad (48)$$

$$Sc_2(S_2O_3)_3 \rightarrow Sc_2(SO_3)_3 + {}^{3}/_{2}S_2 \qquad (49)$$

The elemental sulfur was measured by reaction with silver to form Ag_2S. These secondary reactions begin at temperatures of 300° C for scandium, 700° C for yttrium, and 650° C for lanthanum (CL-001).

Water of hydration causes decomposition of the sulfides. The following equation is an example for scandium (CO-003).

$$Sc_2S_3 + 3H_2O \rightarrow Sc_2O_3 + 3H_2S \qquad (50)$$

The method of decomposing sulfides with water vapor was applied by Schenck and Roters (SC-005) in the preparation of sulfate-free specimens. The sulfate was reduced to sulfide in a H_2 stream at 750° C. Water vapor transforms the sulfide into the oxides.

Suchkov, Borok, and Morozova (SU-002) claim that even a sulfate decomposition in water vapor is possible.

$$Me_x(SO_4)_y + yH_2O \rightarrow Me_xO_y + yH_2SO_4 \qquad (51)$$

This reaction is said to produce concentrated sulfuric acid. The decomposition temperature is said to be lower than that for ordinary thermal decomposition and the reaction is said to be accelerated. Table 15 indicates that lowering of the decomposition temperature was insignificant.

13) Cerium Sulfite

Thermodynamic calculations are not possible for cerium. Experimental results could not be found in the literature. Cerium would be expected to behave like lanthanum and samarium since it has an atomic number of 58, which is between lanthanum (57) and samarium (62). Therefore, decomposition and disproportionation should be competing reactions with appreciable rates at about 300° C.

14) Titanium Sulfite

15) Zirconium Sulfite

Results of Experiments on Decomposition of Sulfates in Water Vapor

Sulfate	Temperature (deg)	Yield η (molar %) after time (minutes)					
		10	20	30	40	50	60
$Ti(SO_4)_2$	400	1.59	2.04	2.24	2.42	2.62	2.80
	500	3.96	6.70	9.31	11.00	12.50	13.92
	600	12.35	24.70	35.80	39.60	42.80	45.50
	700	45.80	63.80	68.00	70.80	72.90	74.80
$FeSO_4$	400	0.12	0.17	0.19	0.22	0.23	0.24
	500	0.75	1.48	2.23	2.80	3.34	3.83
	600	4.65	9.10	13.80	17.50	21.00	24.10
	700	19.00	33.20	45.00	52.00	57.60	62.30
$Cr_2(SO_4)_3$	400	10.02	13.61	15.07	15.97	16.65	17.32
	500	7.00	12.76	17.63	20.75	22.64	23.75
	600	8.80	13.66	16.95	19.70	22.35	24.70
	700	11.09	21.60	32.40	39.40	45.30	48.80
$Al_2(SO_4)_3$	400	0.15	0.27	0.35	0.35	0.35	0.35
	500	0.99	1.25	1.36	1.41	1.46	1.50
	600	2.11	2.80	3.32	3.75	4.13	4.40
	700	5.25	8.70	10.65	11.95	12.90	13.50
	800	18.30	32.00	43.60	53.00	58.00	65.50
$CuSO_4$	600	0.42	0.67	0.74	0.74	0.74	0.74
	700	0.59	1.02	1.32	1.56	1.76	1.92
$MnSO_4$	600	0.19	0.28	0.28	0.28	0.28	0.28
	700	0.38	0.52	0.56	0.59	0.62	0.65
$NiSO_4$	600	0.58	0.86	1.02	1.21	1.38	1.55
$CaSO_4$	1000	0.18	0.34	0.46	0.58	0.71	0.83
$BeSO_4$	500	0.61	1.14	1.66	2.17	2.60	2.85
	600	1.45	2.72	3.50	3.87	4.10	4.20
Na_2SO_4	900	—	—	—	—	—	0.09
	1000	—	—	—	—	—	0.23
K_2SO_4	1000	—	—	—	—	—	0.73
$Sn(SO_4)_2$	200	0.29	0.42	0.53	0.60	0.63	0.65
	250	0.35	0.60	0.84	1.07	1.20	1.25
	300	1.74	3.34	4.82	6.10	7.30	8.00

TABLE 15 - Decomposition of Sulfates with Water Vapor (SU-002)

$$\kappa = \frac{\text{number of moles of } H_2SO_4 \text{ obtained}}{\text{number of moles of } H_2SO_4 \text{ in the original sulfate}} \times 100$$

A. SUCHOV, B. BOROK, Z. MOROZOVA, 'THERMAL DECOMPOSITION OF CERTAIN SULFATES IN A CURRENT OF STEAM,' J. APPL. CHEM. USSR, VOL. 32, P. 1646, (1959).

16) Hafnium Sulfite

Theoretical or experimental data were not available for titanium, zirconium, and hafnium sulfites.

17) Vanadium Sulfite
18) Niobium Sulfite
19) Tantalum Sulfite

Theoretical or experimental data were not available.

20) Chromium Sulfite
21) Molybdenum Sulfite
22) Tungsten Sulfite

Theoretical or experimental data were not available. Chromium oxide does not react with SO_2 at temperatures lower than 400° C (see Section IV).

23) $$4MnSO_3 \rightarrow 3MnSO_4 + MnS \qquad (52)$$

Manganese sulfite shows a tendency to disproportionate in the entire temperature range of interest (see Figure 44).

24) $Mn_2(SO_3)_3$

This compound is not stable at temperatures > 130° C (see figure 12).

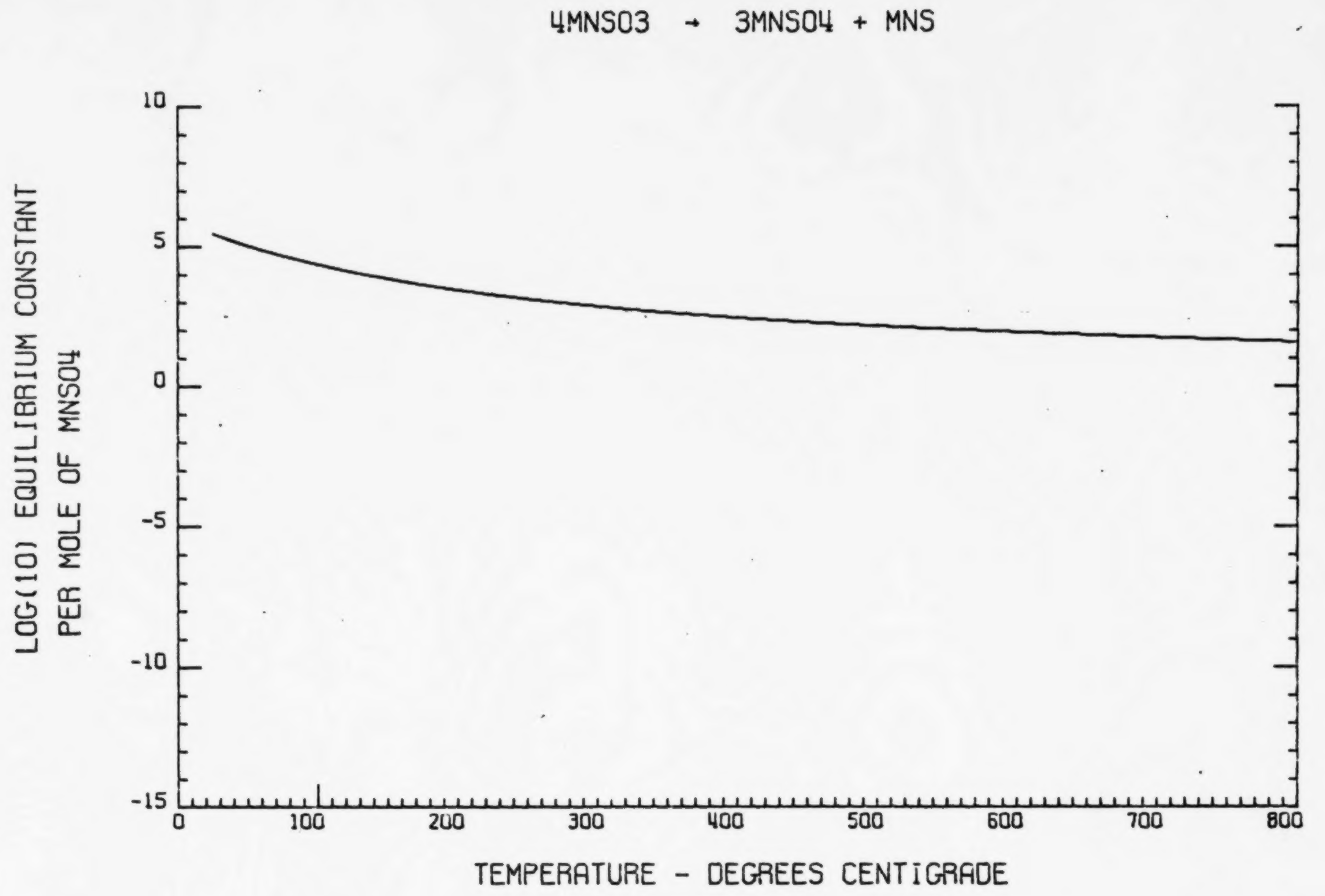

4MNSO3 → 3MNSO4 + MNS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF MNSO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 44

25) Rhenium Sulfite

Theoretical or experimental data were not available.

26) $4FeSO_3 \rightarrow 3FeSO_4 + FeS$ (53)

This compound tends to disproportionate in the entire temperature range (see Figure 45). Experimental data for disproportionation were not given in the literature. Iron oxide does not react with SO_2 at temperatures lower than 400° C (see Section IV).

27) $Fe_2(SO_3)_3$

This compound is thermodynamically unstable at temperatures $> 60°$C (see Figure 14).

28) $4CoSO_3 \rightarrow 3CoSO_4 + CoS$ (54)

Equation 54 is thermodynamically favored in the entire temperature range (see Figure 46). Experimental data for cobalt sulfite were not found in the literature.

29) $4NiSO_3 \rightarrow 3NiSO_4 + NiS$ (55)

Thermodynamic calculations indicated that nickel sulfite disproportionates in the temperature range from 25 to 800° C (see Figure 47).

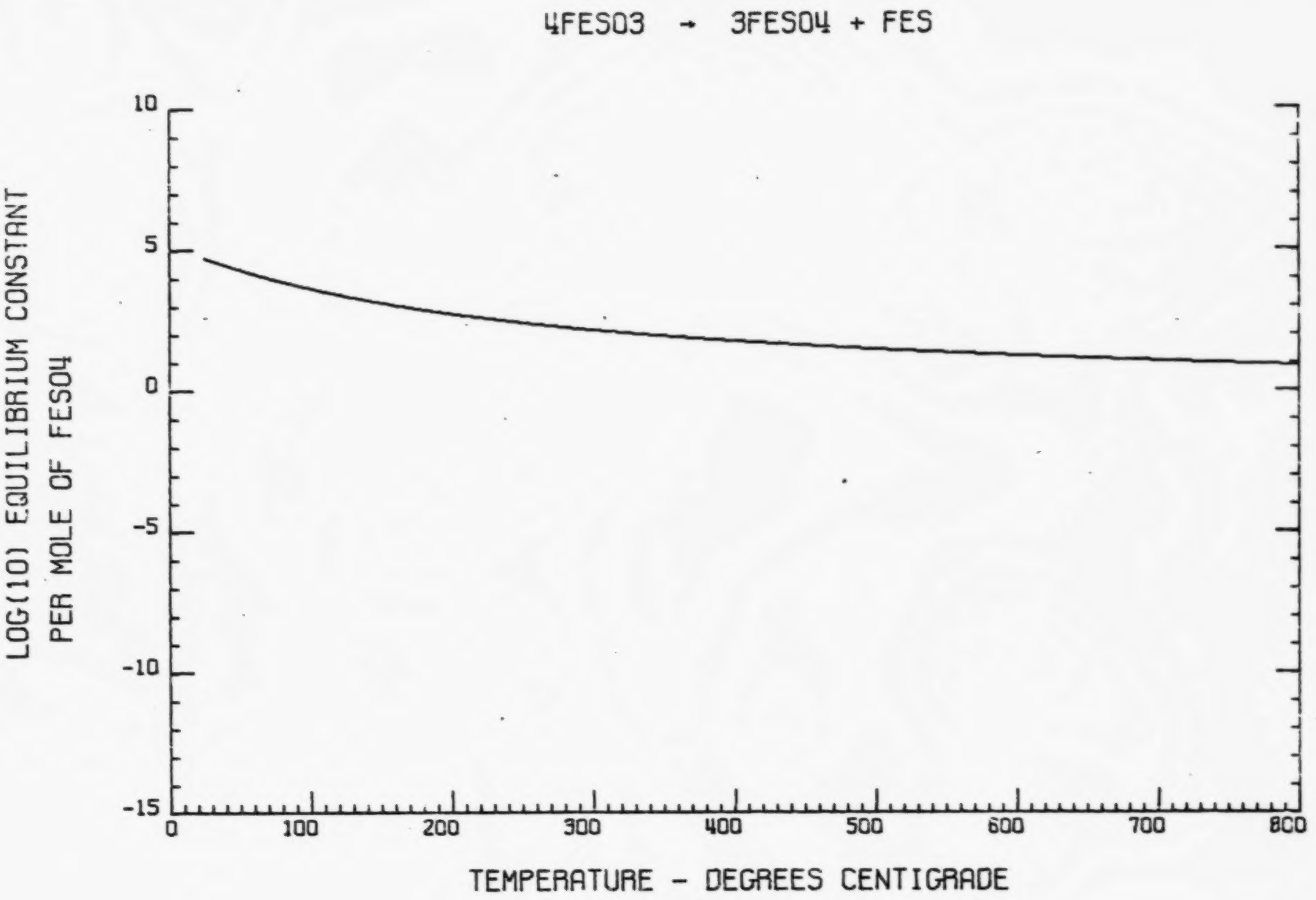

4FESO3 → 3FESO4 + FES
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF FESO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 45

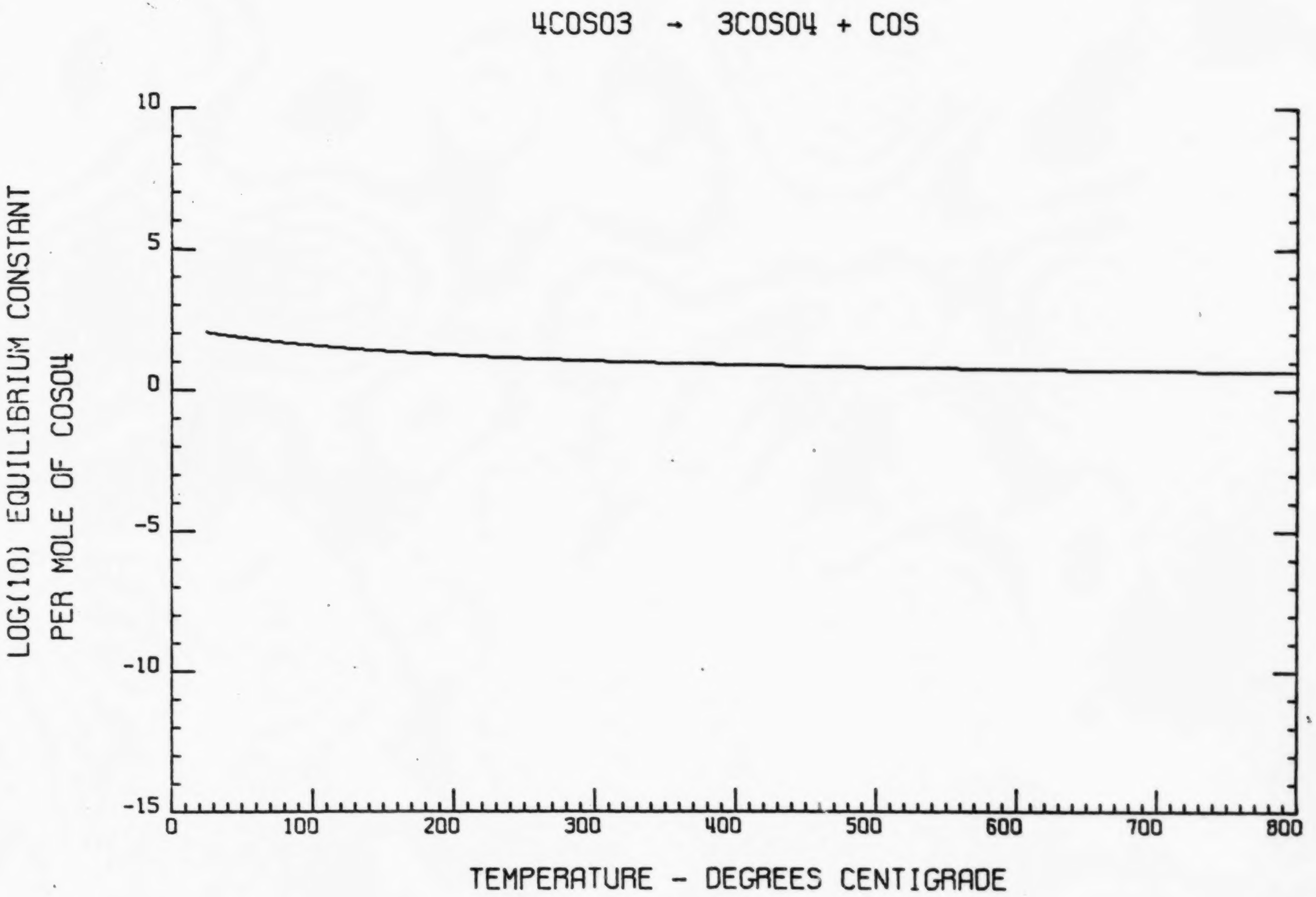


FIGURE 46

12 DEC 68

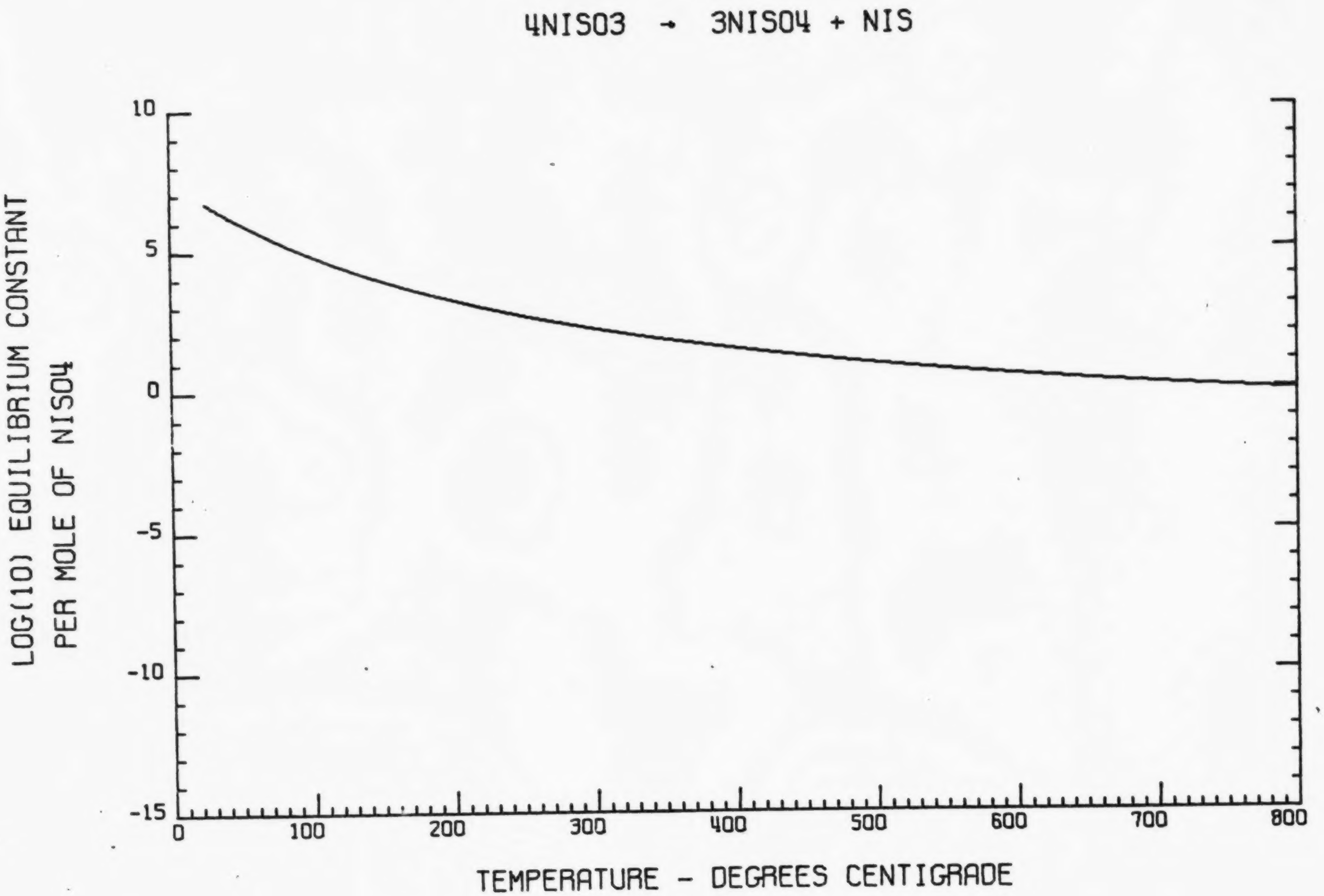

4NISO3 → 3NISO4 + NIS
LOG(10) EQUILIBRIUM CONSTANT PER MOLE OF NISO4
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 47

30) Rhodium Sulfite

31) Iridium Sulfite

32) Palladium Sulfite

Thermodynamic or experimental data were not available.

33) $$4CuSO_3 \rightarrow 3CuSO_4 + CuS \quad (56)$$

According to Figure 48 $CuSO_3$ tends to disproportionate between 25 and 800°C. No experimental data could be found in the literature.

34) $$4Cu_2SO_3 \rightarrow 3Cu_2SO_4 + Cu_2S \quad (57)$$

This compound has a tendency to disproportionate in the entire temperature range of interest (see Figure 49).

35) $$4Ag_2SO_3 \rightarrow 3Ag_2SO_4 + Ag_2S \quad (58)$$

The disproportionation reaction in Equation 58 is also favored thermodynamically in the entire temperature range of interest (see Figure 50). The behavior of Ag_2SO_3 on heating has been investigated by Cola and Castellani Bisi (CO-004). At temperatures above 100°C a decomposition reaction was reported:

$$Ag_2SO_3 \rightarrow 2Ag + \tfrac{1}{2}O_2 + SO_2 \quad (59)$$

At the same time, the remaining Ag_2SO_3 was oxidized by the liberated oxygen. The overall equation is therefore given by Equation 60.

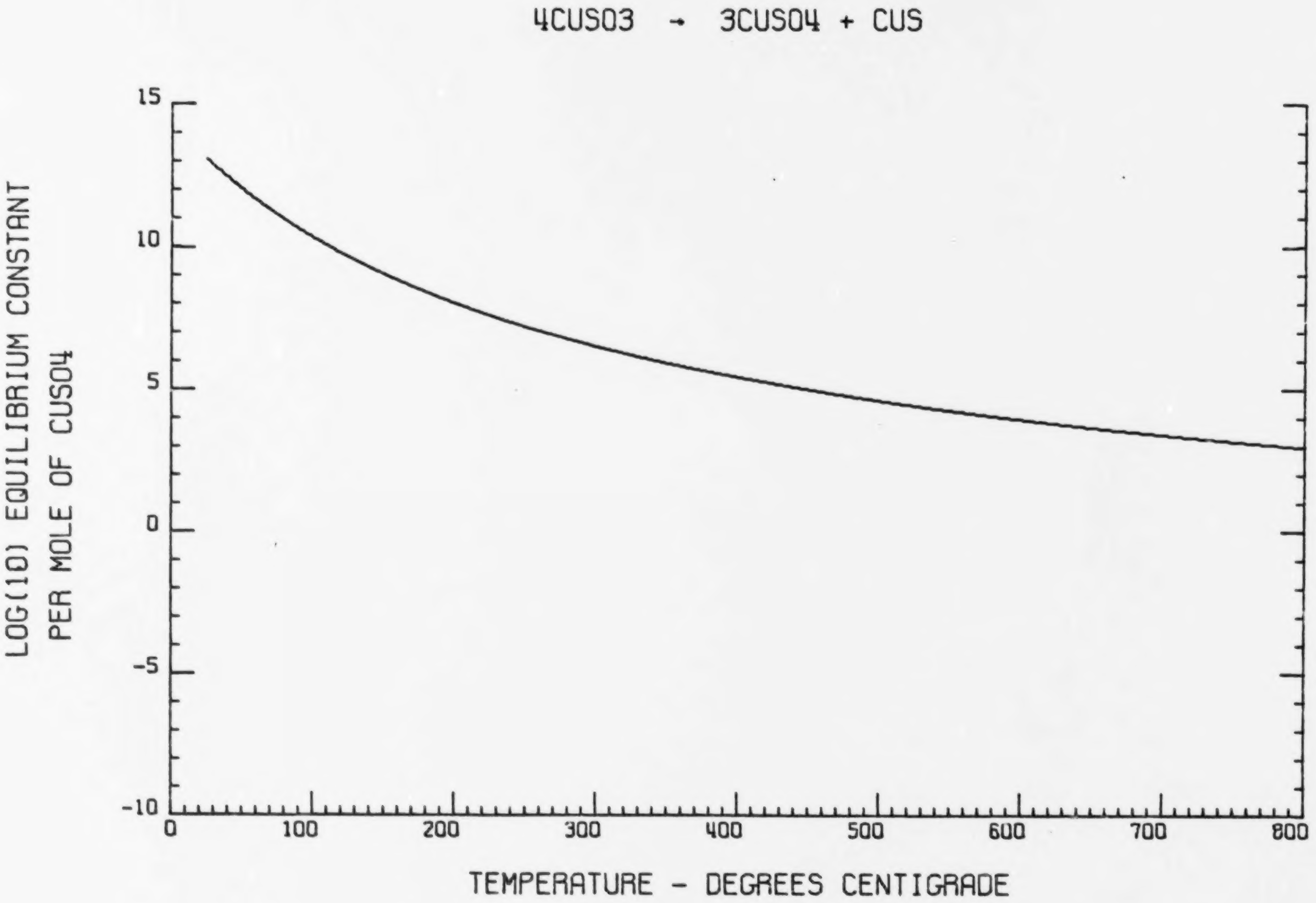


FIGURE 48

12 DEC 68

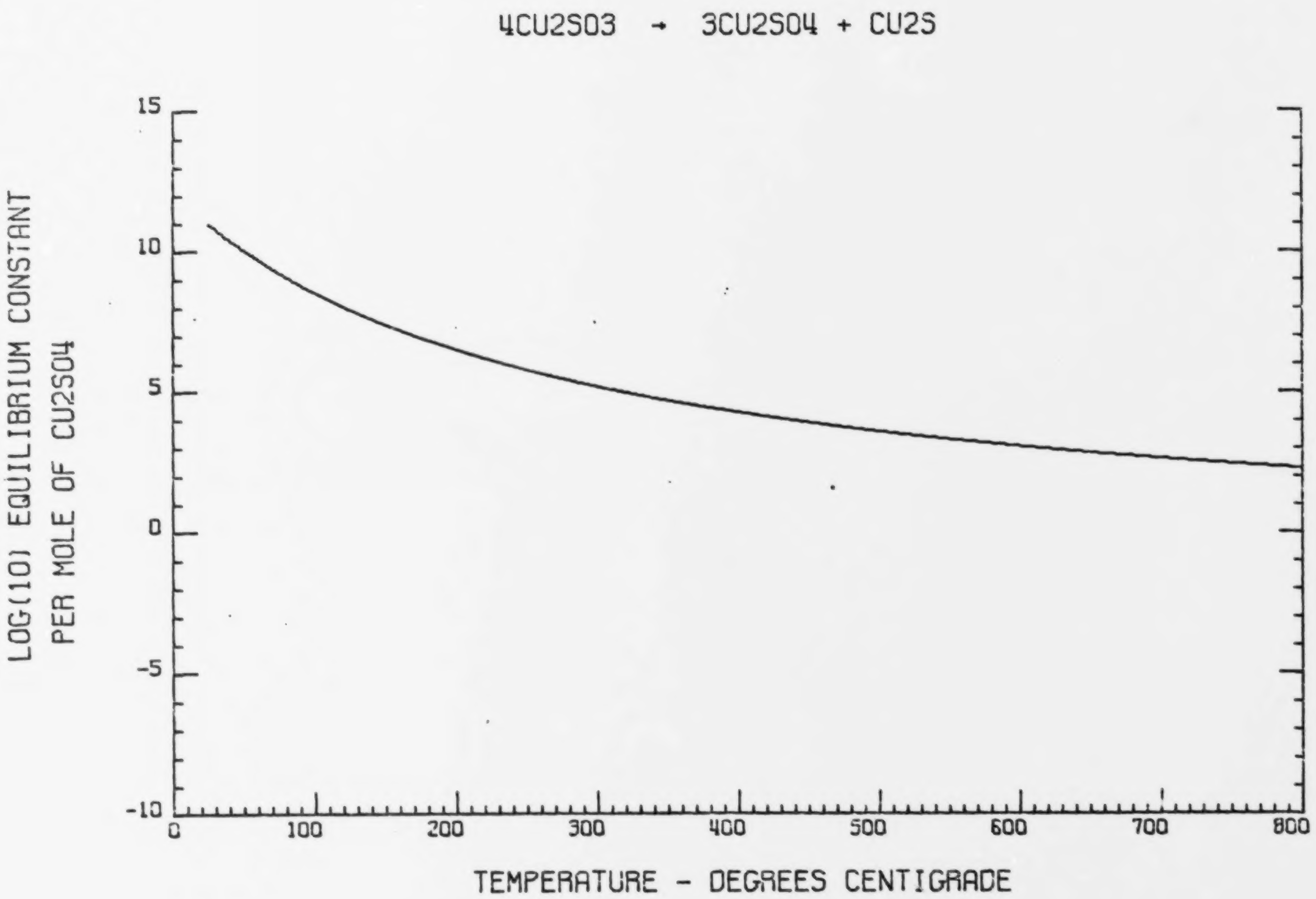


FIGURE 49

16 OCT 68

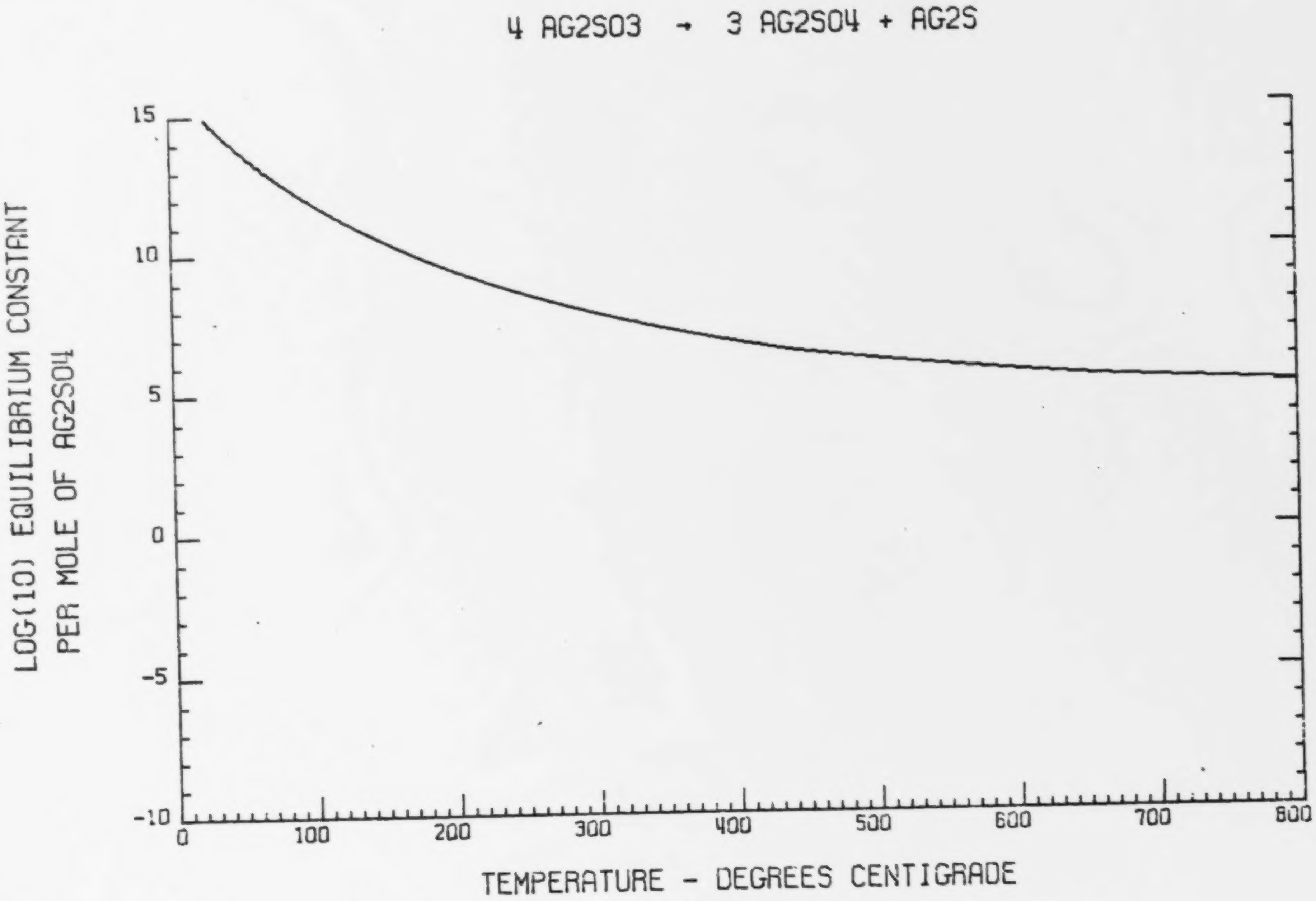

4 AG2SO3 → 3 AG2SO4 + AG2S
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF AG2SO4
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 50

$$2Ag_2SO_3 \rightarrow 2Ag + SO_2 + Ag_2SO_4 \qquad (60)$$

In this case, the decomposition product was the metal, SO_2, and the metal sulfate. Table 16 shows that the ratio of the amount dissociated to the amount oxidized was near 1.0. This supports the overall reaction shown in Equation 60. Decomposition is complete at about 250° C. These results are shown graphically in Figure 51.

ESPERIENZE DI RISCALDAMENTO DI Ag_2SO_3 IN ATMOSFERA INERTE

Temp. °C	Ag_2SO_3 dissociato	Ag_2SO_3 ossidato oxydized	Ag_2SO_3 residuo	Totale
122	tracce	tracce	99,0	
137	0,5	0,6	98,0	99,1
150	8,5	8,7	82,0	99,2
159	18,7	19,2	60,0	97,9
177	40,2	41,0	18,0	99,2
200	48,2	49,0	2,0	99,2
250	50,0	49,5	—	99,5

TABLE 16 - Decomposition and Disproportionation Products of Ag_2SO_3 (CO-004)

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

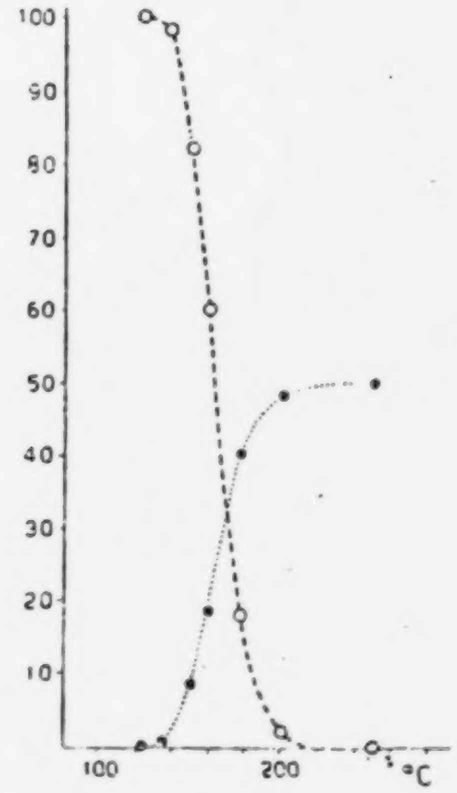


Fig. 1. - Grado di decomposizione di Ag_2SO_3 in corrente di azoto in funzione della temperatura

- - - - Ag_2SO_3 residuo
······ Ag_2SO_3 dissociato (ed ossidato)

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

FIGURE 51 - Thermal Decomposition of Silver Sulfite

Thallium, which exibits a chemical behavior similar to silver, shows the normal disproportionation and decomposition reactions. No elemental thallium was formed. This is shown in Figure 52 and Table 17.

36) $4ZnSO_3 \rightarrow 3ZnSO_4 + ZnS$ (61)

Zinc sulfite tends to disproportionate in the whole temperature range of interest (see Figure 53). The decomposition

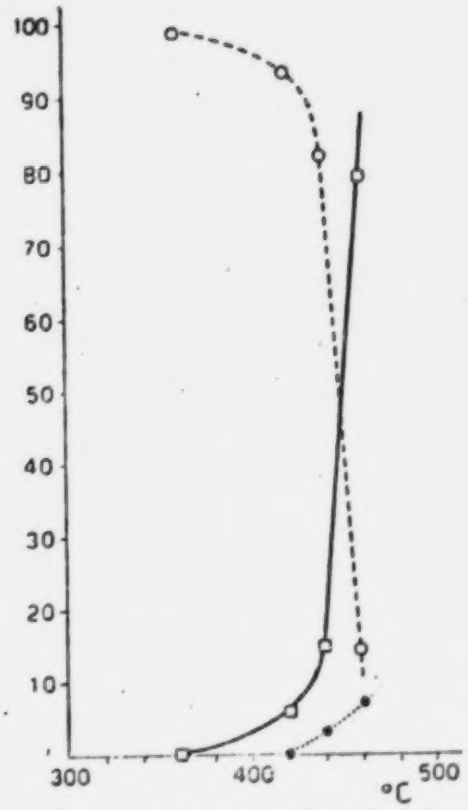


FIG. 2. - Grado di decomposizione di Tl_2SO_3 in corrente di azoto in funzione della temperatura

- - - - - Tl_2SO_3 residuo
——— Tl_2SO_3 dismutato
······· Tl_2SO_3 dissociato

FIGURE 52 - Graphical Representation of the Experimental Results given in Table 17

ESPERIENZE DI RISCALDAMENTO DI Tl_2SO_3 IN CORRENTE DI AZOTO

Temp. °C	Tl_2SO_3 dissociato	Tl_2SO_3 dismutato	Tl_2SO_3 residuo	Totale
360	—	tracce	99,0	99,0
420	tracce	5,8	93,5	99,3
440	3,0	14,7	82,0	99,7
460	6,8	79,6	14,2	100,6

TABLE 17 - Decomposition behavior of Thallium Sulfite

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

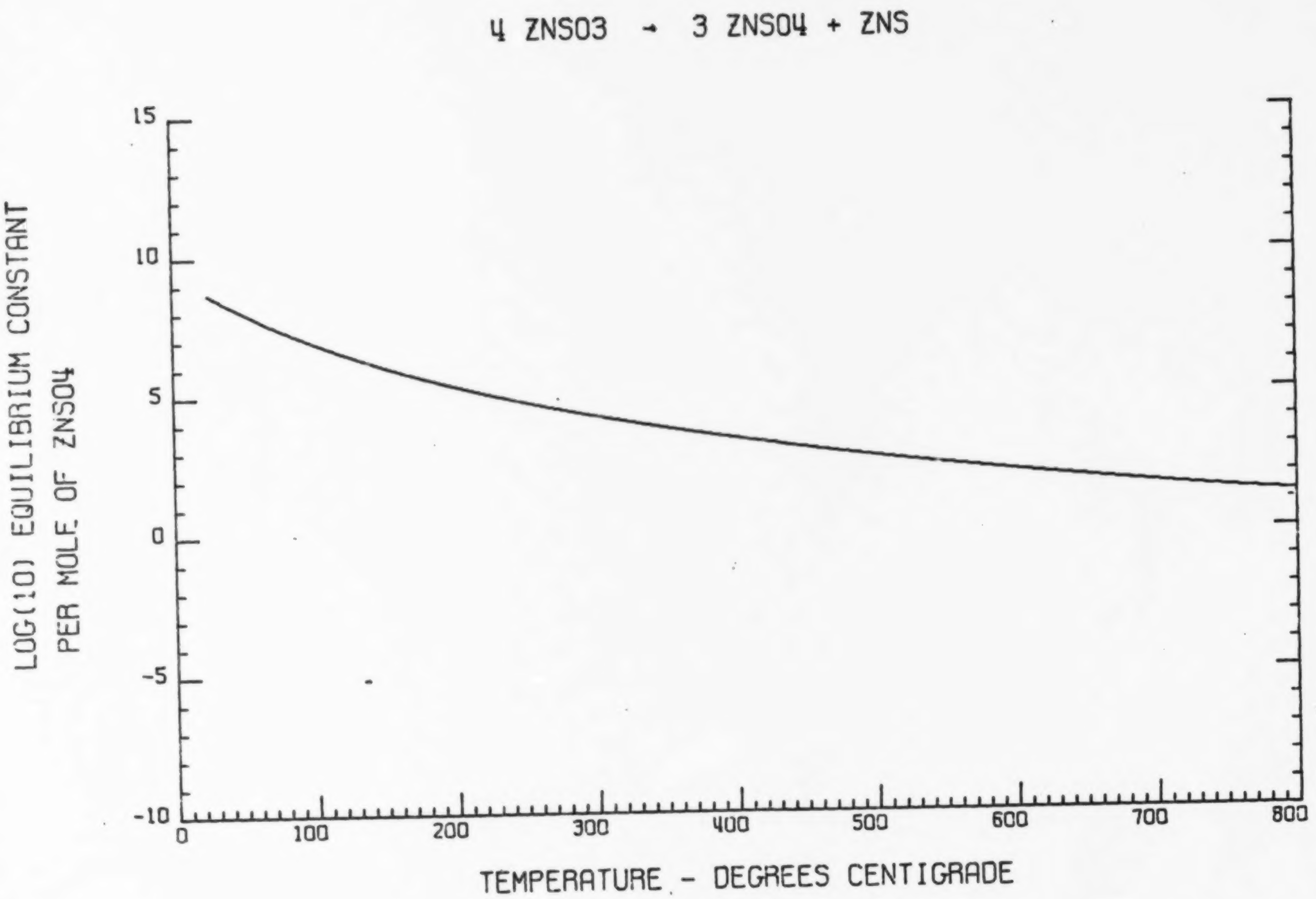


FIGURE 53

25 SEP 66

reaction becomes important since the decomposition point is about 290° C. The decomposition behavior was discussed in detail in our letter report of 14 September 1968.

The experiments of Pechkovskii and Ketov (PE-002), performed in a stream of argon indicated that the disproportionation reaction also took place for zinc, but at a lower rate. The experimental results are shown in Table 18. At 350° C, about 3% of the starting material was converted into sulfates, while 86.72% was decomposed. During the decomposition, a basic sulfite, $ZnO \cdot ZnSO_3$ was formed. This was established by Guy Pannetier (PA-003).

37) $$4CdSO_3 \rightarrow 3CdSO_4 + CdS \qquad (62)$$

$CdSO_3$, like $ZnSO_3$, has the tendency to disporportionate in the whole temperature range under investigation (see Figure 54). Experimental results could not be found in the literature.

38) Boron

No sulfite, sulfate, or carbonate is known.

39) $$4Al_2(SO_3)_3 \rightleftharpoons 3Al_2(SO_4)_3 + Al_2S_3 \qquad (63)$$

Aluminum sulfite, like beryllium sulfite, shows no tendency to disproportionate (see Figure 55). Sorption with sulfite formation, however is not feasible since $Al_2(SO_3)_3$ decomposes at 70° C.

Temperature (°C)	Degree of conversion (in %) of sulfite sulfur into			
	SO_2	ZnS	$ZnSO_4$	total
200	9.34	0.00	0.00	9.34
250	21.32	0.00	0.00	21.32
300	62.25	0.00	0.00	62.25
350	86.72	0.89	2.86	90.47
400	94.04	0.61	1.96	96.66
500	97.32	0.32	1.14	98.78
600	98.11	0.17	0.57	98.85

TABLE 18 - Effect of Temperature on the Degree of Thermal Decomposition of Zinc Sulfite $ZnSO_3 \cdot H_2O$ in a Current of Argon (Duration of each experiment 15 minutes) (PE-002).

V. PECHKOVSKII, A. KETOV, 'A STUDY OF THE THERMAL DECOMPOSITION OF ZINC SULFITE,' J. APPL. CHEM., VOL. 33, PP.1724-9 (1960).

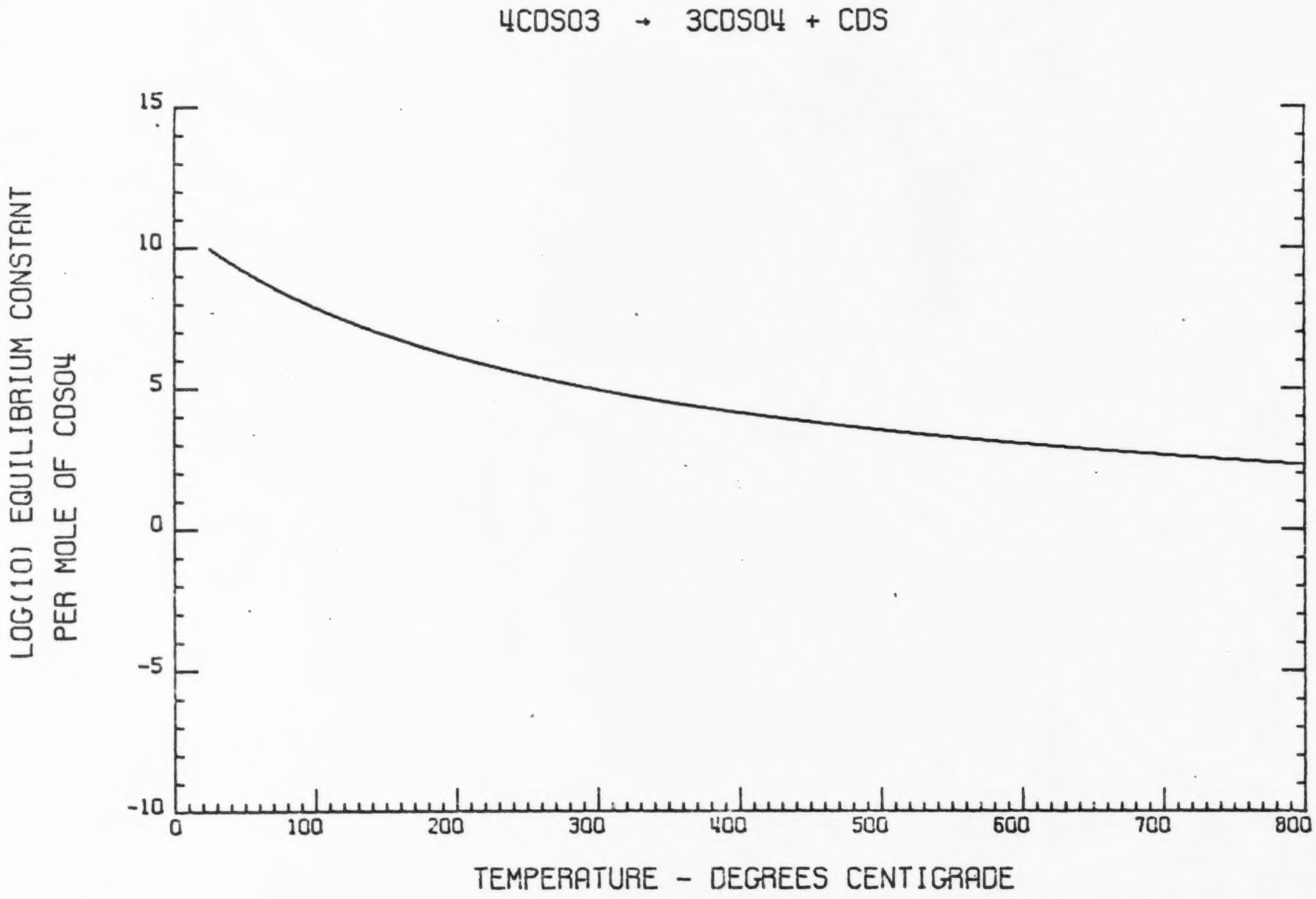


FIGURE 54

17 OCT 68

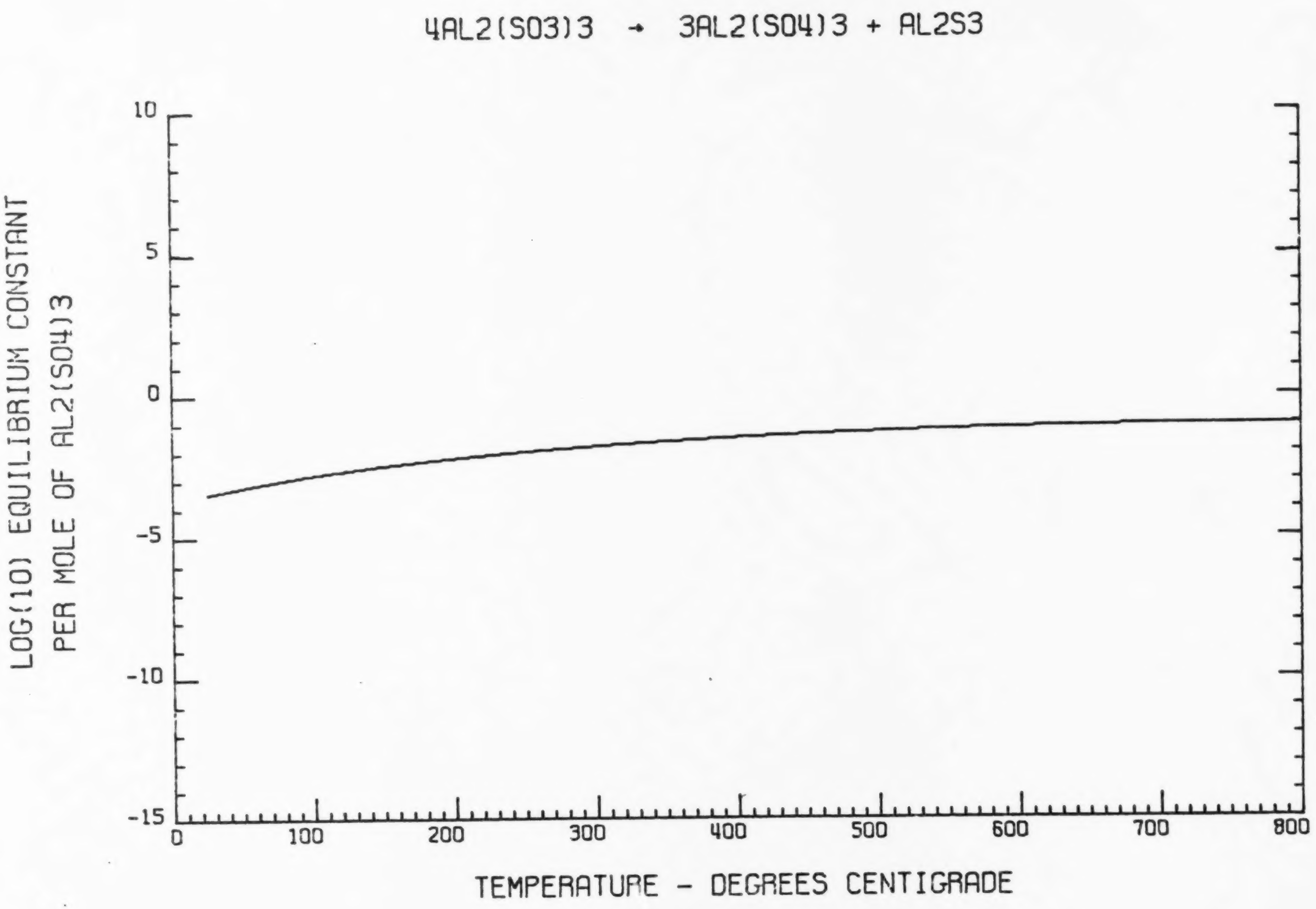

4AL2(SO3)3 → 3AL2(SO4)3 + AL2S3
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF AL2(SO4)3
10
5
0
-5
-10
-15
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 55

40) Gallium Sulfite

41) Silicon Sulfite

42) Germanium Sulfite

Thermodynamic values for these compounds are not known. Experimental data could not be found in the literature.

43) $Sn(SO_3)_2$

This compound is unstable between 25 and 800° C (see Figure 23).

44) $$4PbSO_3 \rightarrow 3PbSO_4 + PbS \qquad (64)$$

Lead sulfite tends to disproportionate in the temperature range of investigation (see Figure 56). For lead sulfite, experimental results describing the decomposition behavior have been published by Castellani and Cola (CO-004). In this case, the experiments were performed in a dynamic atmosphere, as well as under static conditions (autoclave). Tables 19 and 20 show the results of Castellani and Cola. Figure 57 gives a graphic representation. Under both experimental conditions, the disproportionation takes place at an appreciable rate. Under dynamic conditions, however, the percent disproportionation is not nearly as high as in the autoclave experiments.

45) Arsenic

There are no sulfites, sulfates, or carbonates known for arsenic.

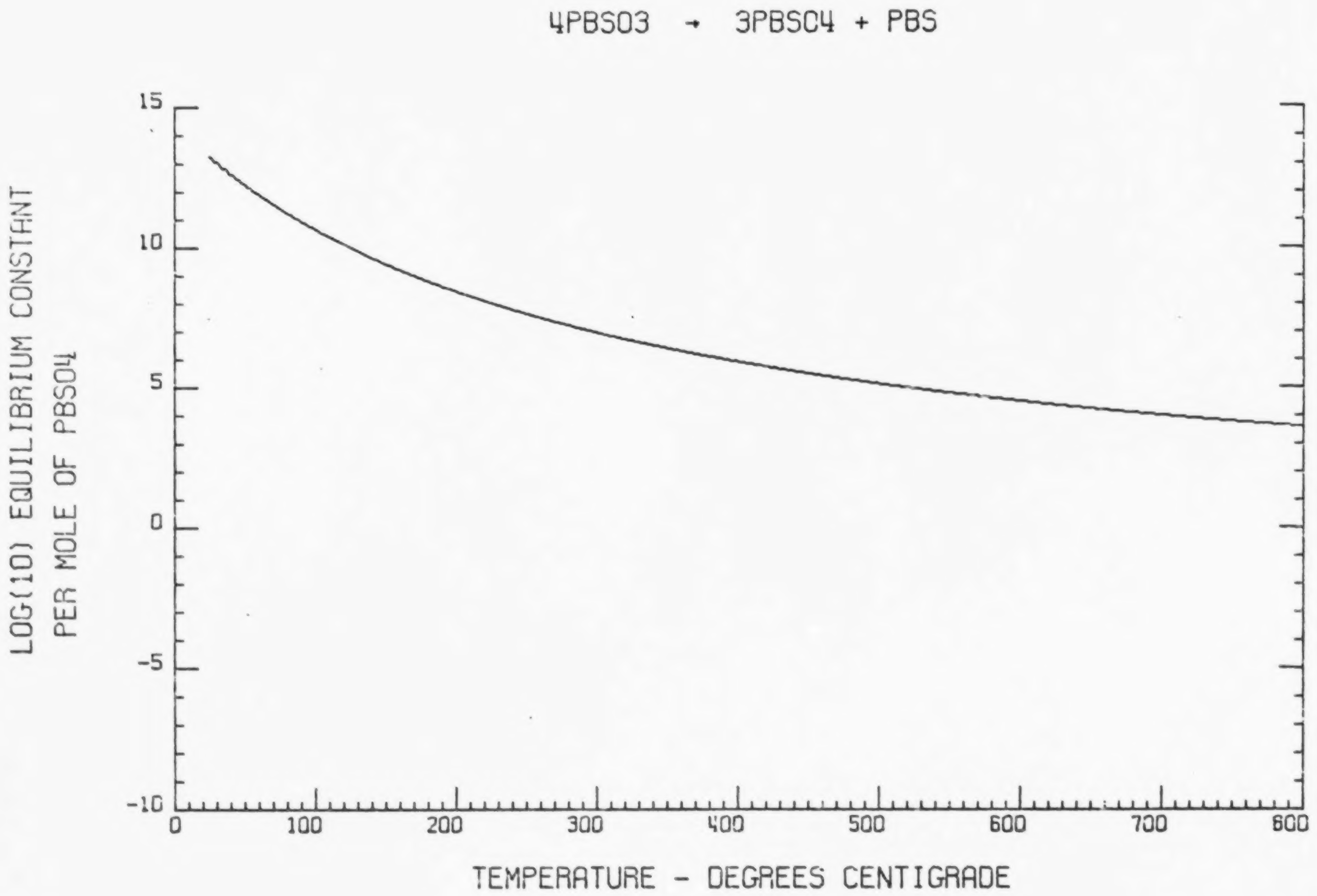

4PBSO3 → 3PBSO4 + PBS
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF PBSO4
15
10
5
0
-5
-10
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

FIGURE 56

ESPERIENZE DI RISCALDAMENTO DI $PbSO_3$ IN CORRENTE DI AZOTO

Temp. °C	$PbSO_3$ dissociato	$PbSO_3$ dismutato	$PbSO_3$ residuo	Totale
311	2,5	3,3	91,9	100.7
331	3,4	6,1	90,5	100,0
356	7,6	11,5	79,6	98,7
398	23,0	19,7	57,4	100.1
460	62,0	31,4	6,6	100,0

TABLE 19 - Decomposition behavior of Lead Sulfite Under Dynamic Conditions (CO-004)

ESPERIENZE DI RISCALDAMENTO DI $PbSO_3$ IN AUTOCLAVE

Temp. °C	$PbSO_3$ dissociato	$PbSO_3$ dismutato	$PbSO_3$ residuo	Totale
315	2,6	2,8	93,4	98.7
373	3,4	5,6	90,0	99,0
380	6,3	10,5	81,8	98,6
403	6,2	63,1	29,9	99,2
430	5,4	89.8	5,7	100.9
460	4,6	94,6	2,4	101,6

TABLE 20 - Decomposition Behavior of Lead Sulfite Under Static Conditions (CO-004)

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

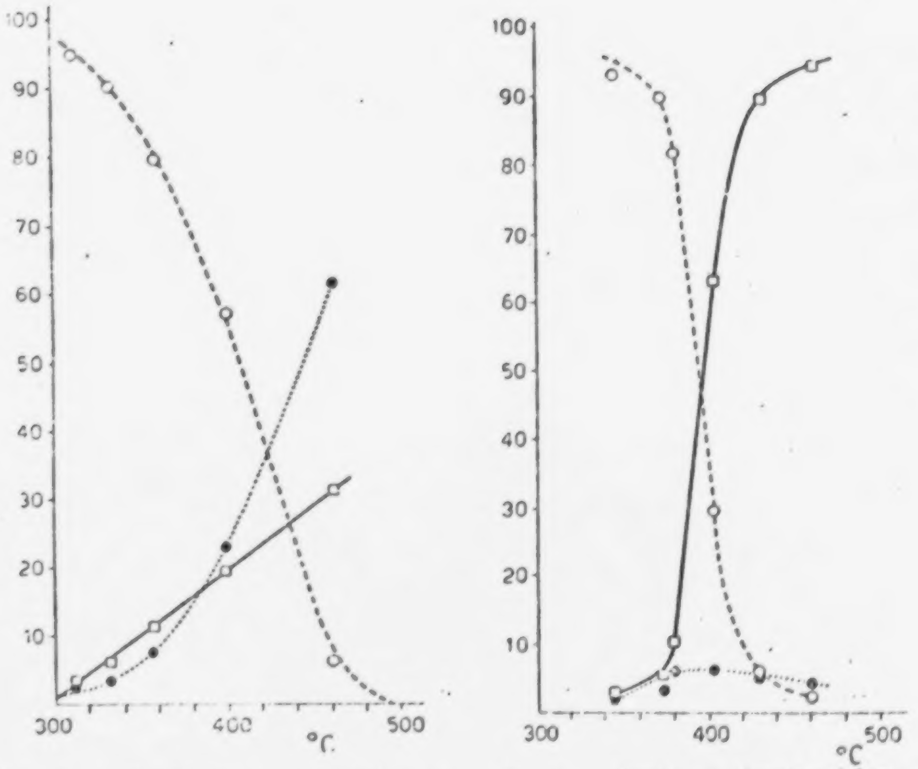


Fig. 5. - Grado di decomposizione di $PbSO_3$ in corrente di azoto in funzione della temperatura

- - - - - $PbSO_3$ residuo
——— $PbSO_3$ dismutato
.... $PbSO_3$ dissociato

Fig. 6. - Grado di decomposizione di $PbSO_3$ in autoclave in funzione della temperatura

- - - - - $PbSO_3$ residuo
——— $PbSO_3$ dismutato
.... $PbSO_3$ dissociato

FIGURE 57 - Comparison of Decomposition and Disproportionation Behavior of $PbSO_3$ under Static and Dynamic Conditions.

M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

46) $Sb_2(SO_3)_3$

This compound is unstable in the temperature range 25 to 800° C (see Figure 25).

47) $4Bi_2(SO_3)_3 \rightarrow 3Bi(SO_4)_3 + Bi_2S_3$ (65)

Figure 58 shows the tendency of $Bi_2(SO_3)_3$ to disproportionate over the entire temperature range. Experimental results describing the decomposition behavior were not found in the literature.

48) $4U(SO_3)_2 \rightarrow 3U(SO_4)_2 + US_2$ (66)

$U(SO_3)_2$ shows no tendency to disproportionate in the range from 25 to 800° C (see Figure 59). Experimental results to confirm or deny this were not in the literature.

49) $4Th(SO_3)_2 \rightarrow 3Th(SO_4)_2 + ThS_2$ (67)

$Th(SO_3)_2$ shows no tendency to disproportionate (see Figure 60). Experimental results to confirm this were not in the literature.

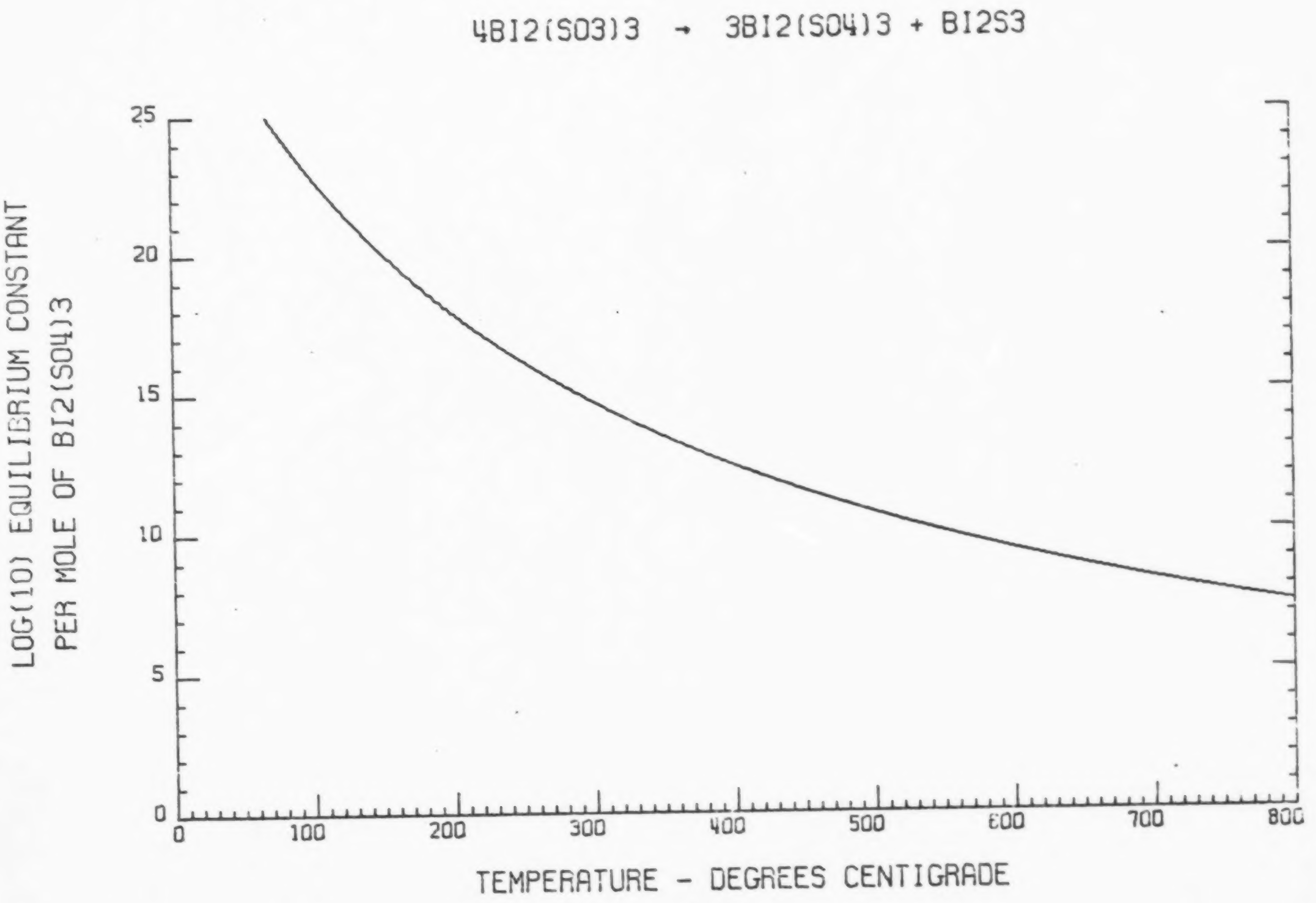


FIGURE 58

16 OCT 68

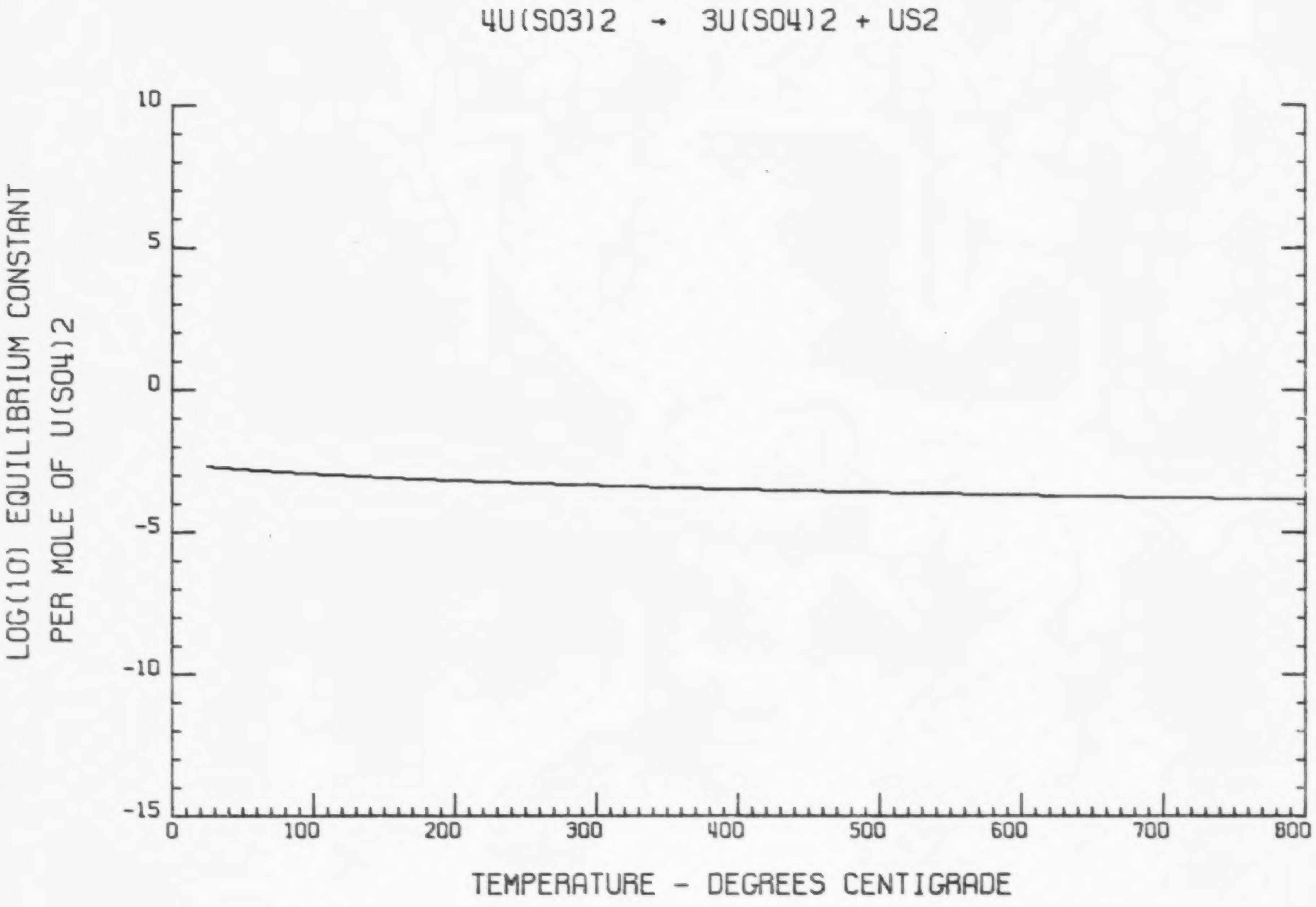


FIGURE 59

12 DEC 68

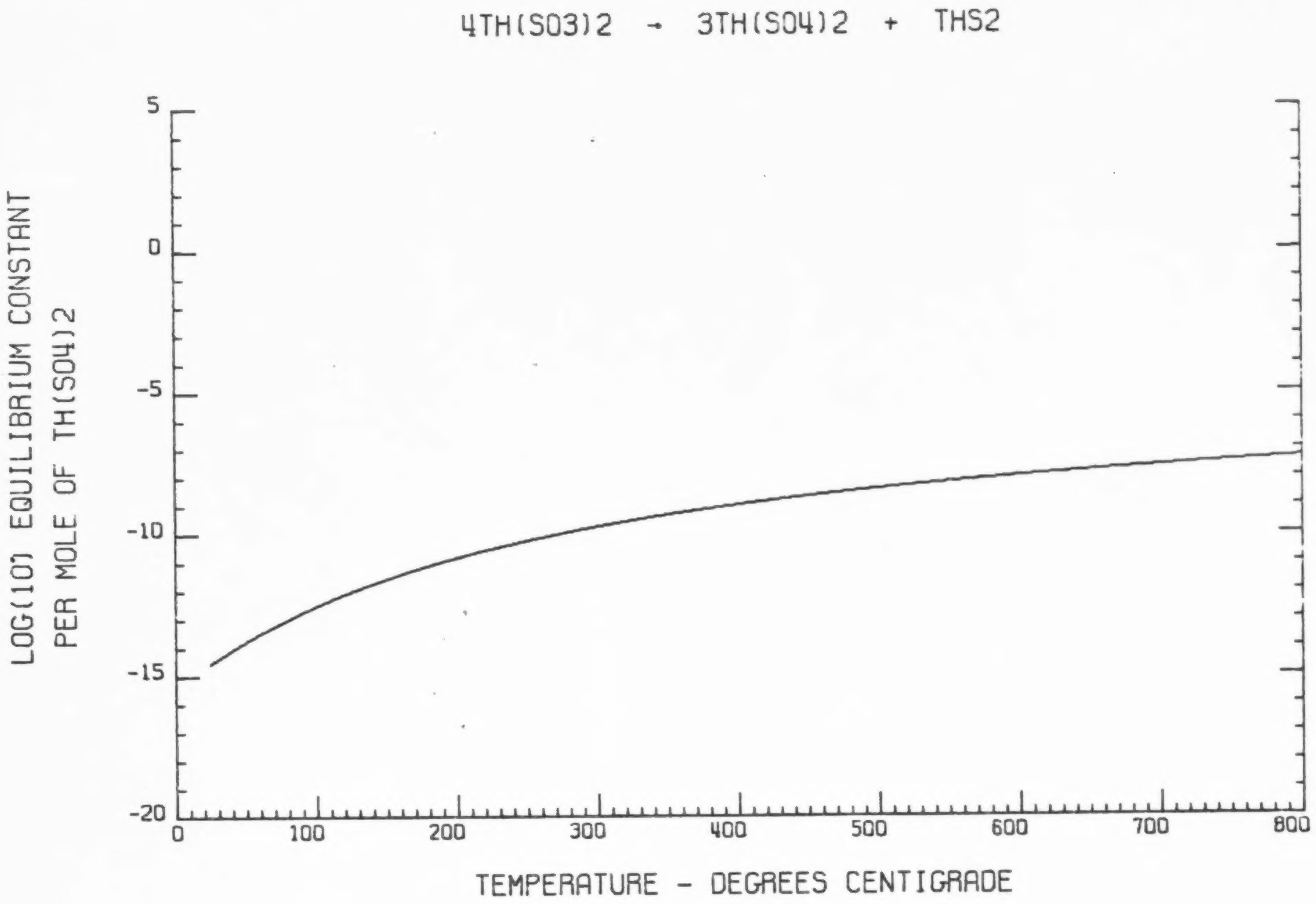


FIGURE 60

12 DEC 68

III. ADSORPTION ON ACTIVE OXIDES WITH SULFATE FORMATION

The problems in sorbing sulfur dioxide on active oxides are closely related to the problem of catalytic activity of a material. The following three steps were proposed to describe the catalytic oxidation of sulfur dioxide on metal oxide catalysts (GM-001).

a) $\text{Oxide}_{\text{lower oxidation state}} + O_2 \rightarrow \text{Oxide}_{\text{higher oxidation state}}$ (68)

b) $\text{Oxide}_{\text{higher oxidation state}} + SO_2 \rightarrow \text{Oxide}_{\text{lower oxidation state}} \cdot OSO_2$ (69)

c) $\text{Sulfate}_{\text{lower oxidation state}} \rightarrow \text{Oxide}_{\text{lower oxidation state}} + SO_3$ (70)

The slowest step in this sequence determines the rate of the catalytic reaction. The main difference between the catalytic oxidation and our problem is that for catalytic oxidation all three steps must be fast steps at the same temperature. This means that a metal oxide could act as a catalyst only in the temperature range where the sulfate is unstable. For sorption and thermal regeneration purposes, however, steps a and b should be fast at the sorption temperature, whereas the sulfate should be stable at the sorption temperature. The principles governing steps a and b in catalytic reactions can, therefore, be applied directly to our problem. The rate of reaction a is of special importance. If reaction a is not thermodynamically favored, sorption with formation of a sulfate is impossible. The rate of step a is influenced by the partial pressure of O_2. The rate of reaction c is influenced by the partial pressure of SO_3 in the gas phase. For the catalyst to be effective, the O_2 partial pressure must be equal to or greater than the partial pressure of the oxide pair and the SO_3 partial pressure in the gas phase must be equal to or less than that of the sulfate intermediate. It is not possible to calculate reaction rates from thermodynamic quantities. Thomson (NE-001), however, gives the following rule of thumb: the reaction rates are high when there is a low heat of reaction involved, and vice versa.

Eucken (EU-001) gave the following scheme for the heats of reaction and activation energies involved in catalytic SO_2 oxidation.

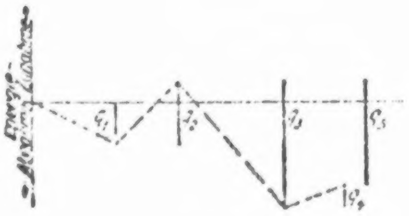


Fig. 3

FIGURE 61 - Energy Diagram for the Catalytic Oxidation of SO_2 (EU-001).

A. EUCKEN, LEHRBUCH DER CHEM. PHYS., LEIPZIG, (1930), P.627.

The following symbols are used:

q_1 heat of reaction for:

Oxide$_{\text{lower oxidation state}}$ + O_2 → Oxide$_{\text{higher oxidation state}}$

+ heat of adsorption of SO_2

q_2 Heat of activation for the oxide in the higher oxidation state

q_3 heat of reaction for:

activated oxide in the higher oxidation state + sorbed SO_2 → sulfate intermediate

q_4 heat of dissociation for:
sulfate intermediate → oxide in lower oxidation state + SO_3

q_5 overall heat of reaction for Equation 71:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \qquad (71)$$

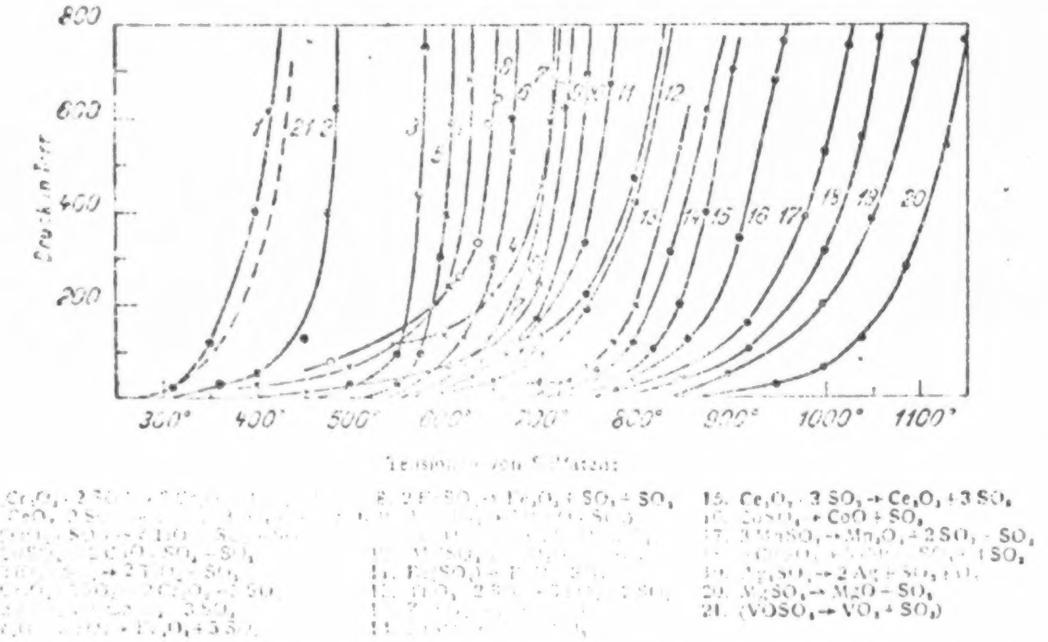
Therefore, a good catalyst fulfills the following conditions:

a) The oxidation of the oxide in the lower oxidation state must be a fast step and the O_2 partial pressure for the oxide pair must be high. This means a low heat of reaction is involved, and q_1 is, therefore, small. For a given system, the oxygen partial pressure may sometimes be raised by diminishing the particle size on an atomic scale or by the addition of promoters.

b) The sulfate intermediate in the lower oxidation state must be formed quickly.

c) The dissociation of the sulfate intermediate must be a fast step. The SO_3 tension of the sulfate intermediate at the reaction temperature must be high. The sulfate of the metal could do one of several things, namely 1) dissociate to SO_3 and oxide, 2) oxidize to form a sulfate of the metal in a higher oxidation state, or 3) form a basic sulfate. The first alternative is the desirable one. The second and third reactions could take place if the sulfate compounds of alternatives two or three were more stable than that of alternative one.

In Figure 62 the SO_3 partial pressures are given for several systems (GM-001).



L. GMELIN, GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE, SULFUR, PART A PP. 324-51 (1953).

FIGURE 62 - SO_3 Partial Pressures of Sulfates (GM-001)

Schenck (SC-006) and Schmahl (SC-007) established the following rules for mixed oxides, or catalysts composed of more than one oxide component.

a) A decrease in the O_2 pressure takes place 1) when the oxide in the higher oxidation state forms a mixed crystal, 2) when a chemical compound is formed with the oxide in the higher oxidation state, or 3) when the particle size increases.

b) An increase takes place when the added oxide reacts with the oxide in the lower oxidation state.

An example of this is the cupric oxide-cuprous oxide system. The partial pressure of this system is increased by the addition of Cr_2O_3 which forms a chromite with the lower oxidation state. Consider the reactions:

$$2CuO \rightarrow \tfrac{1}{2}O_2 + Cu_2O \qquad \Delta G_1 \qquad (71a)$$

$$2CuO + Cr_2O_3 \rightarrow \tfrac{1}{2}O_2 + Cu_2Cr_2O_4 \qquad \Delta G_2 \qquad (71b)$$

$$Cu_2O + Cr_2O_3 \rightarrow Cu_2Cr_2O_4 \qquad \Delta G_3 \qquad (71c)$$

Since reaction 71c was gotten by subtraction of the first two reactions, the relationship between free energy changes may be expressed as follows:

$$\Delta G_2 = \Delta G_1 + \Delta G_3 \qquad (71d)$$

For a reaction such as the formation of mixed oxide compounds from the component oxides, the entropy of reaction is small. Therefore, the free energy change is approximately equal to the enthalpy change. Hence:

$$\ln P_{O_2}{}_{Cr_2O_3\,\text{added}} = \ln P_{O_2}{}_{CuO} - \frac{\Delta H^R}{RT} \qquad (71e)$$

Since ΔH^R must be negative in order for the mixed oxide to have formed, it may be seen that the oxygen partial pressure was increased. A similar argument showed that if the more stable mixed oxide had been $CuCr_2O_4$, then the oxygen partial pressure would have been decreased.

A decrease in oxygen partial pressure took place in the PbO_2, PbO, O_2 system when alkali oxides were added (SC-005). This was due to the formation of stable plumbates.

In comparing the catalytic activity of several compounds in different oxidation reactions (oxidation of CO, H_2, and SO_2) with the O_2 pressure and the heat of activation, R. Schenck found the following relation (SC-008):

"The energy of activation of a catalyst is inversely proportional to the logarithm of its O_2 pressure."

The O_2 pressure of an oxide pair is a very important quantity in the sorption step, along with the SO_3 tension of the sulfate. With this rule, one can predict from thermodynamic calculations whether or not an oxide system is a potential sorbent which forms a sulfate as a reaction product. With the assumption that a catalytic gas-solid reaction tends to reach equilibrium, one can calculate the maximum degree of conversion possible.

The equilibrium in Equation 72,

$$2SO_3 \rightleftharpoons 2SO_2 + O_2 \tag{72}$$

can be described as follows:

$$K_p = \frac{P_{O_2} \cdot (P_{SO_2})^2}{(P_{SO_3})^2} \tag{73a}$$

or

$$P_{O_2} = K_p \cdot \left(\frac{P_{SO_3}}{P_{SO_2}}\right)^2 \tag{73b}$$

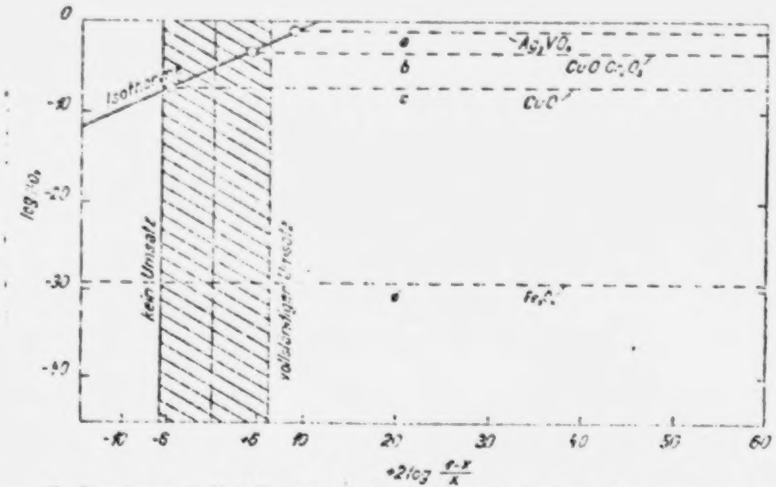
or

$$\ln P_{O_2} = \ln K_p + 2 \cdot \ln\left(\frac{1-x}{x}\right) \qquad (73c)$$

In equation 73c, x is the fraction of sulfur as SO_2.

In a diagram with $2 \cdot \ln(\frac{1-x}{x})$ as abscissa and log P_{O_2} as ordinate, Equation 73c is represented by a straight line for a given temperature. Figure 63 shows this for the temperature T = 527° C.

Fig. 39.



O_2-Tension von Metallverbb. als Maß ihres katalyt. Oxydationsvermögens.

FIGURE 63 - Degree of SO_2 Conversion as a Function of the Oxide Partial Pressure of the Catalyst

R. SCHENCK, 'KATALYTISCHE WIRKSAMKEIT UND GLEICHGEWICHT,' Z. ANORG. CHEM., VOL. 260, PP.154-60(1949).

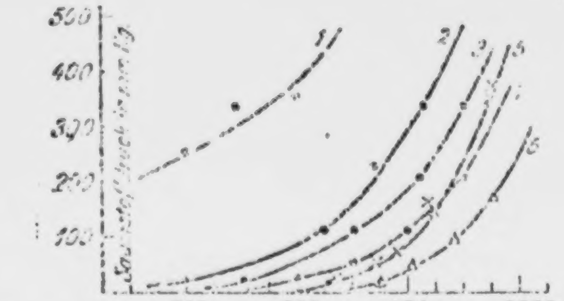
The oxygen partial pressure over an oxide system is a horizontal line for a univariant system at a given temperature. In a closed system with SO_3, SO_2, and O_2 in the gas phase in equilibrium with two solid oxide phases, the O_2 partial pressure in the gas phase will have the same value as the partial pressure of the solid oxide pair. The $SO_2 \rightarrow SO_3$ conversion will take place until the quantity $2 \cdot \ln(\frac{1-x}{x})$ has reached the value given by the intersection with the horizontal isotherm plotted in Figure 63. From the oxide systems described in Figure 63, only CuO and $CuO \cdot Cr_2O_3$ can provide a conversion within the shaded area. A higher degree of conversion can be expected with Ag_3VO_4 and a lower one with Fe_3O_4. This fact gives us the following criteria for the selection of potential sorbents:

a) The SO_3 pressure of the most stable sulfate or oxisulfate must be low enough to guarantee a maximum SO_3 concentration of only 150 ppm in the exit flue gas.

b) The oxygen partial pressure over the oxide system should be high enough to assure that the oxide will be in its higher oxidation state. For oxides, such as nickel, that can dissolve significant quantities of oxygen, the problem is not as clear cut.

c) The oxide system should be thermally regenerable. This fact will probably limit the number of useful oxides. For instance, PbO_2 and MnO_2 have a great enough oxidation power and sorption capability. These oxides cannot, however, be regenerated in air. Only strong oxidizing agents are able to oxidize the lower oxides to this high oxidation state. In the Monsanto process, the oxidation of Mn^{++} is performed in aqueous solutions since the manganese is easily oxidized in alkaline solutions.

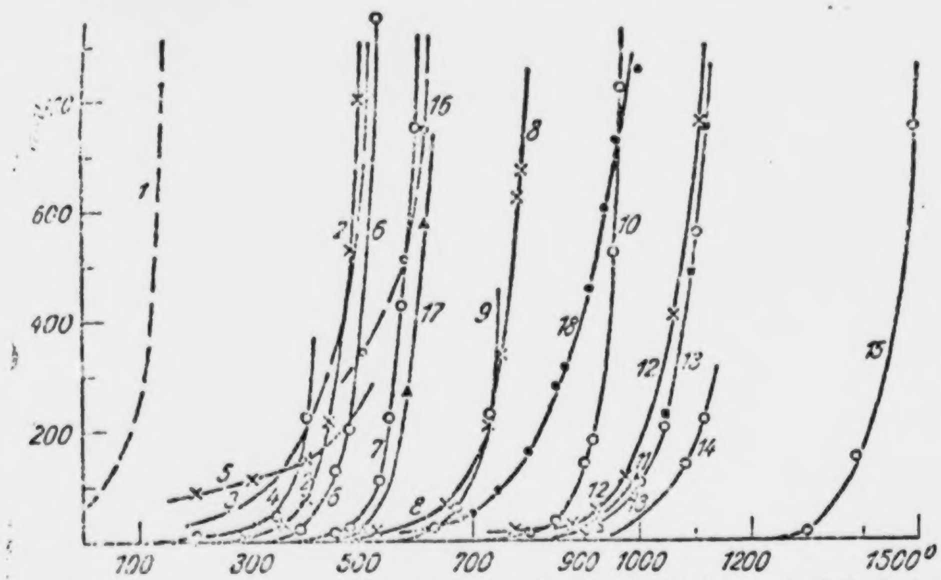
Another fact that makes the compound selection difficult is that the O_2 partial pressure, which has been shown to be so important in the sorption step, depends on the way the oxide is prepared. Figure 64 shows this for MnO_2 specimens prepared in different ways (KR-003). The reason for the different results was the fact that MnO_2, as well as cobalt, nickel, and uranium oxides, showed a great solubility of oxygen in the lattice. When such systems are decomposed thermally, they are divariant until the compound $Me_xO_y \cdot zO$ is transformed to Me_xO_y.



C. KROGER, 'ZUR HETEROGENEN KATALYSE BINARER GASREAKTIONEN,'
Z. ANORG. CHEM., VOL. 235, PP. 369-97 (1932).

FIGURE 64 - Oxygen Partial Pressure Over MnO_2 Prepared Using Different Methods (KR-003)

According to the rule of Schenck, an oxide system should react at a lower temperature the higher the oxygen partial pressure. Figure 65 shows the partial pressure over some oxide systems as a function of temperature (KR-003).



1. Ag_2O/Ag; 2. HgO/Hg; 3. $Co_3O_4 \cdot mO_2/Co_3O_4$; 4. Sb_2O_5/Sb_6O_{13}; 5. CaO_2/CaO; 6. MnO_2/Mn_2O_3; 7. Pb_3O_4/PbO; 8. BaO_2/BaO; 9. Sb_6O_{13}/Sb_2O_4; 10. Co_3O_4/CoO; 11. RuO/Ru; 12. Rh_2O_3/Rh; 13. CuO/Cu_2O u. RhO/Rh_2O; 14. Sb_2O_4/Sb_2O_3; 15. Fe_2O_3/Fe_3O_4; 16. UO_2/U_3O_8 17. $UO_{2.8}/U_3O_8$ 18. Mn_2O_3/Mn_3O_4

FIGURE 65 - Oxygen Partial Pressure Over Oxide Pairs as a Function of Temperature (KR-003)

C. KROGER, 'ZUR HETEROGENEN KATALYSE BINARER GASREAKTIONEN,'
Z. ANORG. CHEM., VOL. 235, PP. 369-97 (1932).

In Table 21 (KR-003), the oxide systems were ordered according to the heats of reaction for Equation 75. One recognizes that the lower the starting temperature for reaction 74, the lower the heat of reaction for Equation 75:

$$\begin{array}{l}\text{Oxide in higher oxidation state} + H_2 \text{ or } CO \\ \rightarrow \text{Oxide in lower oxidation state} + H_2O \text{ or } CO_2\end{array} \qquad (74)$$

$$\begin{array}{l}\text{Oxide in lower oxidation state} + O_2 \\ \rightarrow \text{Oxide in higher oxidation state}\end{array} \qquad (75)$$

According to Table 21 and Figure 65 it is obvious that Ag_2O, CaO_2, PbO_2, CrO_3, MnO_2, NiO_2, BaO_2, and HgO have the best oxidation power and should sorb SO_2 easily. Preliminary experiments in our laboratory showed that this was true.

There is some disagreement in the literature concerning the order of strength as an oxidizing agent. C. Kröger gave the following order (KR-003): $Ag_2O > MnO_2 > Co_3O_4 > Ni_xO_y > CuO$. F. Benton (BE-001) gave the following order: $Co_2O_3 > CuO > MnO_2 > Fe_2O_3$. According to Frazer (FR-002, FR-003), one can prepare a sample of MnO_2 so active that it oxidizes carbon monoxide at room temperature with 100% efficiency. The order of Kröger, therefore, seems to be the most reasonable. The reason that different investigators reported inconsistent results was probably due to different methods of compound preparation. It is known that oxygen has a high solubility in oxides of cobalt (LE-001), nickel (LE-002), and uranium (HU-009, GO-002, BI-004). For instance, a highly active cobalt oxide was prepared by decomposition of $Co(NO_3)_2 \cdot 6H_2O$ at 200 to 300°C. It had excellent sorption behavior

Tabelle 1

Dissoziationsprod.	Ag	CaO	(PbO)	Cr_2O_3	Mn_2O_3	NiO	BaO	Hg_2	Hg	CoO	Mn_3O_4	V_2O_4	(MoO_2)	Cu_2O	Cu	Tl	(Bi)	(As)	(Sb)
Oxyd	Ag_2O	CaO_2	PbO_2	CrO_3	MnO_2	NiO_2	BaO_2	Hg	Hg_2O	Co_3O_4	Mn_2O_3	V_2O_5	MoO_3	CuO	Cu_2O	Tl_2O	Bi_2O_3	As_2O_3	Sb_2O_3
Bildungswärme pro O-Atom	5,1 7,0	5,4 11,0	12,6	12,2	14,4 13,0		18,4	20,0	22,2	24	25,2 27,0	28,2	32,8	37,7 39,0	40,8 43,8	42	45,9	51,5	54,3
Reaktionsbeginn mit H_2	34°		140—160 189	185	105 188			50; 75 115; 90	80 140	207	(230)		(300)	140 150—194	155			185	
mit CO	0° −20°		80	15	30			0; 20 96	20		(240)			60 125—146	110				

Dissoziationsprod.	Pb	Co	(Ni)	Ni	MnO	Fe_3O_4	FeO	Fe	(WO_2)	(Ti_2O_3)	(Ce_2O_3)	W	SnO	Sn	Zn	Mn	(CrO)	(Cr)	(Al)
Oxyd	PbO	CoO	NiO	Ni_2O	Mn_3O_4	Fe_2O_3	Fe_3O_4	FeO	WO_3	TiO_2	CeO_2	WO	SnO_2	SnO	ZnO	MnO	Cr_2O_3	Cr_2O_3	Al_2O_3
Bildungswärme pro O-Atom	50,5 52,9	57,5	58,6		55,2	61,4	(73,7)	64,0	63,5			65,2	70,5	67,0 70,0	84,8	90,8		89,3	125
Reaktionsbeginn mit H_2	185° 211°, 235°	165 197, 228	194 230	270 339	296	287 (350)	305	370				280			310 454				
mit CO	160° 185°	155	120			202 220	200												

TABLE 21 - Starting Temperatures for CO and H_2 Oxidation in Comparison with Heat of Reaction for Change in Oxidation State of the Catalyst (KR-003)

C. KROGER, "ZUR HETEROGENEN KATALYSE BINARER GASREAKTIONEN," Z. ANORG. CHEM., VOL. 205, PP. 369-97 (1932).

in the 350 to 400° C range. However, when the sulfate was decomposed at about 850° C, the product was an oxide which was inactive in the 350 to 400° C range but became active at temperatures of 500 to 600° C.

IV. CATALYTIC OXIDATION OF SO_2

When sorption occurs on metal oxides with sulfite formation there is a possibility of disproportionation in the thermal regeneration step. For sorption on active metal oxides with sulfate formation two requirements must be fulfilled. The active metal oxide must have a high enough oxidation power and the sulfate must have a favorable SO_3 partial pressure. These two restrictions reduce the number of potential adsorbents.

It has been shown that some of the requirements for activity of an oxide as a catalyst are the same as those necessary for the sorption of SO_2 when accompanied by sulfate formation. The properties of a catalyst and a potential sorbent differ mainly in the SO_3 partial pressure of the sulfate. At the temperature at which the oxide used as a catalyst is effective, its sulfate must be unstable. On the other hand, for a sorbent at the sorption temperature, the stability of the sulfate is a basic requirement.

It was shown in T.M. 004-009-Ch8 that the alkali metal and alkaline earth sulfates are too stable for thermal regeneration. Therefore, for single oxides the transition metal oxides are the only remaining potential sorbents. These metal oxides are known to be catalytically effective as SO_2 oxidation catalysts. Two ideas have been revealed. First, an oxide that is effective as an SO_2 oxidizing catalyst is unsuitable as a sorbent in the temperature range in which it is catalytically effective, since it's sulfate is unstable at that temperature. Second, the oxides which are poor catalysts because of the formation of a stable sulfate are potential sorbents.

The following is a literature survey of the catalytic behavior of transition metal oxides. Most of the fundamental work was done in the 1930's. The efficiency of the metal oxides or mixtures of oxides was compared in these works with the conversion capability of platinum. In the experiments of Neumann, et al., who published most of the work a gas mixture of the following composition was used in all experiments:

$$7\%\ SO_2;\ 19.53\%\ O_2;\ 73.47\%\ N_2.$$

The catalysts investigated were placed in a tube two centimeters in diameter. The length of the catalyst bed was about 20 cm. The streaming rates of the gas mixture were 150 and 300 cm^3/min.

Platinum (NE-002)

The platinum was precipitated on asbestos. Table 22 gives the degree of conversion as a function of temperature. The results are plotted in Figure 66 along with the results of Knietsch who used a mixture with a lower O_2 concentration (7% SO_2, 10% O_2, 83% N_2, dotted line).

TABLE 22

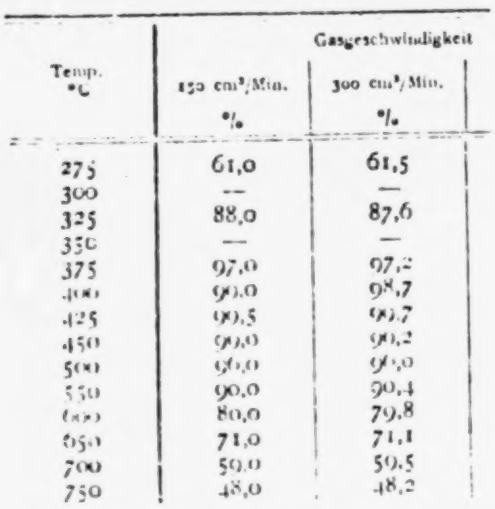


Tabelle 1.

Temp. °C	Gasgeschwindigkeit 150 cm³/Min. %	300 cm³/Min. %
275	61,0	61,5
300	—	—
325	88,0	87,6
350	—	—
375	97,0	97,2
400	99,0	98,7
425	99,5	99,7
450	99,0	99,2
500	96,0	96,0
550	90,0	90,4
600	80,0	79,8
650	71,0	71,1
700	59,0	59,5
750	48,0	48,2

FIGURE 66

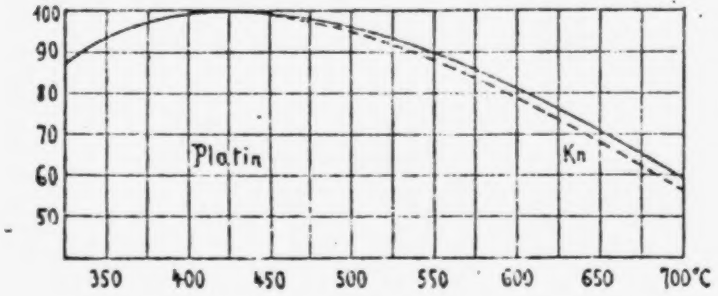


Fig. 2.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 595-734 (1928).

The conversion was practically the same for both streaming rates (150 and 300 ccm/min.). The optimum conversion temperature was 425° C.

Silver vanadate-Ag_3VO_4 (NE-002)

Silver vanadate was proposed for use as a catalyst in a German patent (FA-001). Next to platinum, it is the most effective catalyst known for the SO_2 conversion.

Neumann prepared the catalyst in the following way: 14.1 g V_2O_5 were dissolved in Na_2CO_3 solution. The solution was filtered and diluted with water to 250 ml. Then 20 g of asbestos (free of iron) were moistened with 25 cm^3 of the above solution. 39.5 ml of a 10% $AgNO_3$ solution were added. A yellow-red precipitate was formed on the asbestos. It was dried at 120° C. Finally the asbestos contained 5% Ag_3VO_4. Table 23 and Figure 67 show the degree of conversion.

TABLE 23

Temp.	Gasgeschwindigkeiten pro Minute							
	A. 150 cm^3		B. 300 cm^3		C. 500 cm^3		D. 750 cm^3	
°C	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge
325	82,5	93,9	73,0	83,1	59,0	67,2	—	—
375	92,0	94,7	84,5	87,0	73,5	75,7	57,0	58,7
425	96,5	96,9	90,5	90,9	82,0	82,3	72,0	72,3
450	97,0	97,9	92,0	92,8	84,0	84,8	76,0	76,7
465	97,0	98,5	92,5	93,9	85,0	86,3	78,5	79,7
475	96,5	98,5	92,5	94,4	85,5	87,2	79,0	80,6
487,5	96,0	99,0	92,0	94,8	86,0	88,4	80,5	83,0
500	95,0	99,0	91,0	94,8	85,5	89,0	81,0	84,1
507	94,7	99,2	90,5	94,8	85,0	89,0	81,0	84,8
525	92,0	98,4	90,0	96,2	85,0	90,9	80,5	86,1
550	88,0	97,5	87,0	96,4	84,0	93,1	79,5	88,1

FIGURE 67

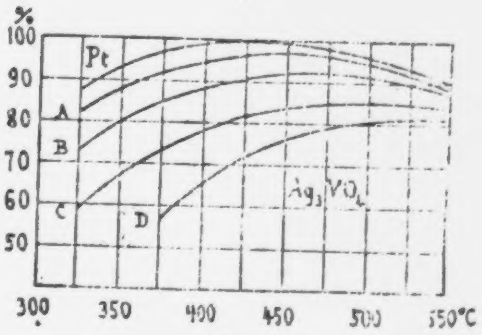


Fig. 3.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 695-734 (1928).

Table 23 and Figure 67:

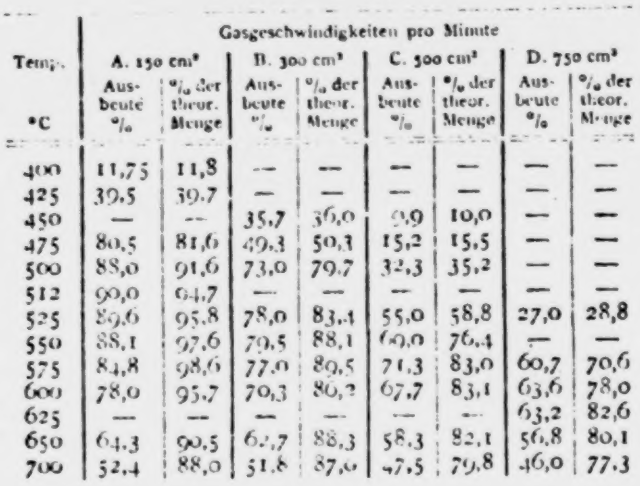
Conversion of SO_2 to SO_3 over Ag_3VO_4 on asbestos. 7% SO_2, 19.53% O_2, 73.47% N_2. Steaming rates 150 (A), 300 (B), 500 (C), and 750 (D) cm^3/min. As apposed to platinum, the percent conversion with a steaming rate of 300 cm^3/min is lower than that with 150 cm^3/min.

Vanadium-Pentoxide-V_2O_5 (NE-002)

Vanadium pentoxide as a catalyst for the SO_2-SO_3 conversion was proposed in two German patents (FI-001, BA-002). One method of catalyst preparation was the decomposition of ammonium vanadate supported by pumice stone at 440° C.

Neumann prepared the catalyst in the following way: 7 g V_2O_5 were mixed with pumice stone powder of a grain size of 2-5 mm. The mixture was moistened with water, mechanically mixed and dried at a slightly elevated temperature (exact data not given). The results are summarized in Table 24 and Figure 68.

TABLE 24



Temp.	Gasgeschwindigkeiten pro Minute							
	A. 150 cm^3		B. 300 cm^3		C. 500 cm^3		D. 750 cm^3	
°C	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge
400	11,75	11,8	—	—	—	—	—	—
425	39.5	39.7	—	—	—	—	—	—
450	—	—	35.7	36,0	9,9	10,0	—	—
475	80,5	81,6	49.3	50,3	15,2	15,5	—	—
500	88,0	91,6	73,0	79.7	32,3	35,2	—	—
512	90,0	94,7	—	—	—	—	—	—
525	89,6	95.8	78,0	83,4	55,0	58,8	27,0	28,8
550	88,1	97,6	79.5	88,1	69,0	76,4	—	—
575	84,8	98,6	77,0	89,5	71,3	83,0	60,7	70,6
600	78,0	95.7	70,3	86,2	67,7	83,1	63,6	78,0
625	—	—	—	—	—	—	63,2	82,6
650	64,3	90,5	62,7	88,3	58,3	82,1	56,8	80,1
700	52,4	88,0	51,8	87,0	47,5	79,8	46,0	77.3

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 695-734 (1928).

FIGURE 68

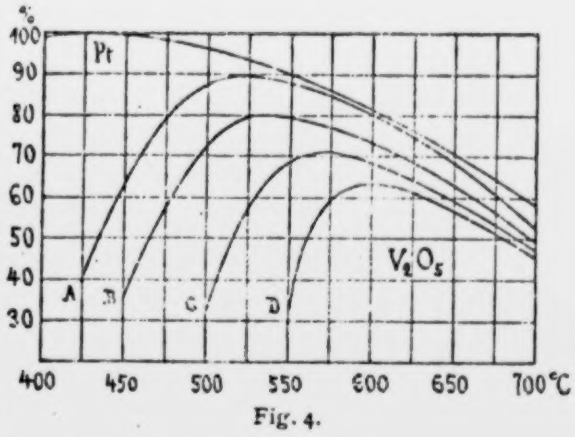


Table 24 and Figure 68:

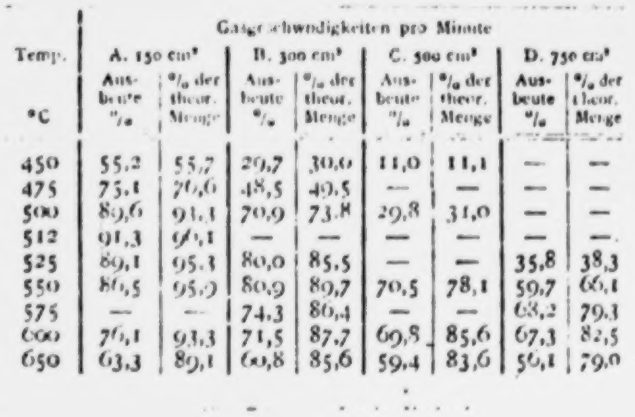
SO_2 conversion over V_2O_5 on pumice stone. 7% SO_2, 19.53% O_2, 73.47% N_2. Streaming rates 150 (A), 300 (B), 500 (C), and 750 cm^3/min.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 696-734 (1928).

At temperatures under 400° C, the conversion was practically zero. The color of the V_2O_5 during the experiment turned from red-brown at the start to gray-green at the end. This indicates that reduction took place.

Copper-Vanadate: $Cu_3(VO_4)_2$ (NE-002)

The use of copper-vanadate was proposed in a German patent (KU-006). With copper vanadate precipitated on pumice stone, the results as shown in Table 25 and Figure 69 were obtained.



Temp. °C	Gasgeschwindigkeiten pro Minute							
	A. 150 cm³		B. 300 cm³		C. 500 cm³		D. 750 cm³	
	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge	Ausbeute %	% der theor. Menge
450	55,2	55,7	29,7	30,0	11,0	11,1	—	—
475	75,1	76,6	48,5	49,5	—	—	—	—
500	89,6	91,1	70,9	73,8	29,8	31,0	—	—
512	91,3	96,1	—	—	—	—	—	—
525	89,1	95,3	80,0	85,5	—	—	35,8	38,3
550	86,5	95,9	80,9	89,7	70,5	78,1	59,7	66,1
575	—	—	74,3	86,4	—	—	68,2	79,3
600	76,1	93,3	71,5	87,7	69,8	85,6	67,3	82,5
650	63,3	89,1	60,8	85,6	59,4	83,6	56,1	79,0

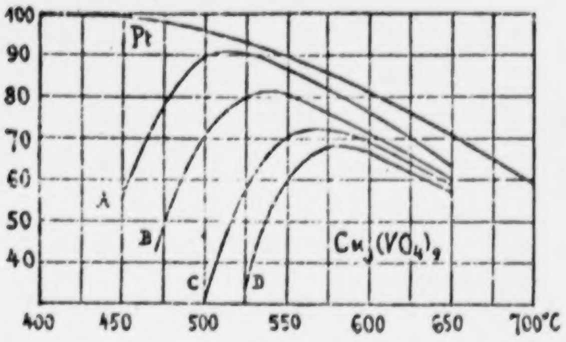


Fig. 5.

Table 25 and Figure 69:

SO_2 conversion over $Cu_3(VO_4)_2$ on pumice stone. 7% SO_2, 19.53% O_2, 73.47% N_2.

Streaming rates: 150 (A), 300 (B), 500 (C), and 750 cm^3/min.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 695-734 (1928).

Comparing the results with these of V_2O_5 shows that $Cu_3(VO_4)_2$ does not improve the degree of conversion.

Sodium metavanadate $NaVO_3$ (NE-003)

The catalyst was prepared by moistening and mixing sodium metavanadate with diatomaceous earth. The results obtained with this catalyst are plotted in Figure 70 (small circles) together with the conversion on pure V_2O_5 (large circles). The plot also shows the degree of conversion found with commercial vanadium catalysts. It is surprising that the conversion power of the commercial catalysts lies in the same range as that for sodium-metavanadate. Neumann pointed out that due to the method used in preparing the commercial vanadium catalyst, there is always a possibility that some sodium vanadate was also formed.

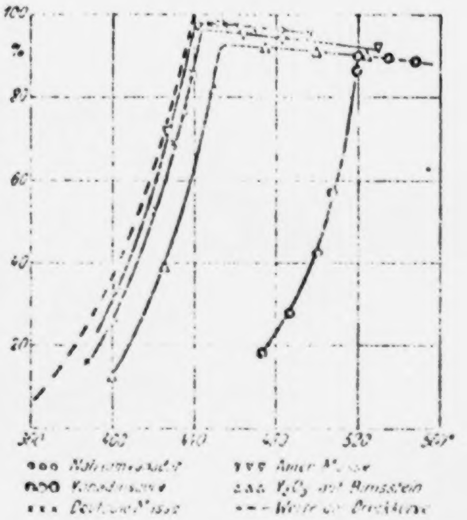


Fig. 3.

FIGURE 70

SO_2 conversion over $NaVO_3$ on diatomaceous earth.

7% SO_2, 19.53% O_2, 73.47% N_2.

Streaming rate ltr/hr

○○○ Sodium metavanadate

○○○ Pure V_2O_5

xxx German catalyst

▽ American catalyst

△ V_2O_5 on pumice stone

--- P_{SO_3} equilibrium pressure for the system $NaVO_3$ - SO_2

B. NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, VI.,' Z. ELECTROCHEM., VOL. 41, PP. 589-93 (1935).

Calcium Vanadate $Ca(VO_3)_2$ (NE-003)

Calcium vanadate was reported by H. N. Holmes and A. L. Elder (HO-001) to have extremely good catalytic properties. At temperatures above 460° C, they reported conversions better than those obtained with platinum (See Figure 71).

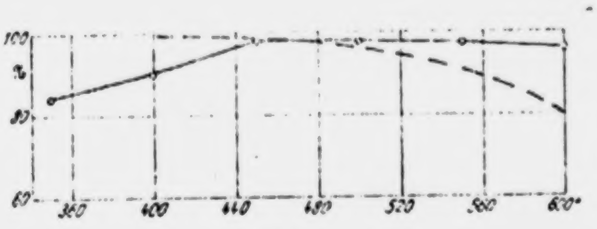


Fig. 4.

FIGURE 71
Oxidation of SO_2 over $Ca(VO_3)_2$ (Holmes and Elder, HO-001)

H. N. HOLMES. A. L. ELDER, IND. ENG. CHEM., VOL. 22, P. 471 (1930).

Neumann checked these results. The calcium vanadate was precipitated on balls of diatomaceous earth. After equilibrium was reach the calcium metavanadate showed only the same conversion as V_2O_5. During the test $Ca(VO_3)_2$ decomposed with formation of $CaSO_4$ and V_2O_5. Figure 72 shows the results of Neumann (NE-003).

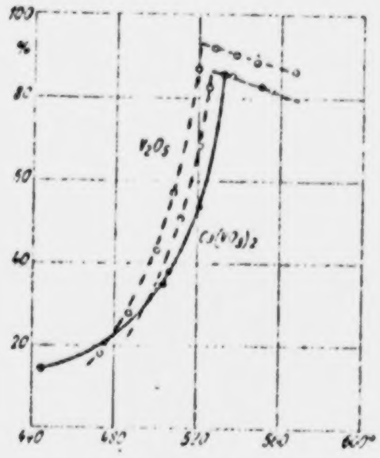


Fig. 5.

FIGURE 72

Oxidation of SO_2 to SO_3 over calcium metavanadate on diatomaceous earth. 7% SO_2, 19.53% O_2, 73.47% N_2. Streaming rate 10 ltr/hr.
B. NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE , VI.,' Z. ELECTROCHEM., VOL. 41, PP. 589-93 (1935).

Thermodynamic calculations by TRACOR agree with the results of Neumann. The free energy of the reaction (See Figure 72a) favors the formation of $CaSO_4 + V_2O_5$ at all temperatures below 800° C.

Silver (NE-002)

Silver catalyst was prepared by carefully washing 10 g of asbestos with hydrochloric and nitric acids, then moistening with $AgNO_3$, drying and decomposing the nitrate by heating. The asbestos contained five percent Ag. The reaction tube was filled with this contact catalyst spread over a length of 15 cm. The total amount of silver was 0.53 g. The following results were obtained:

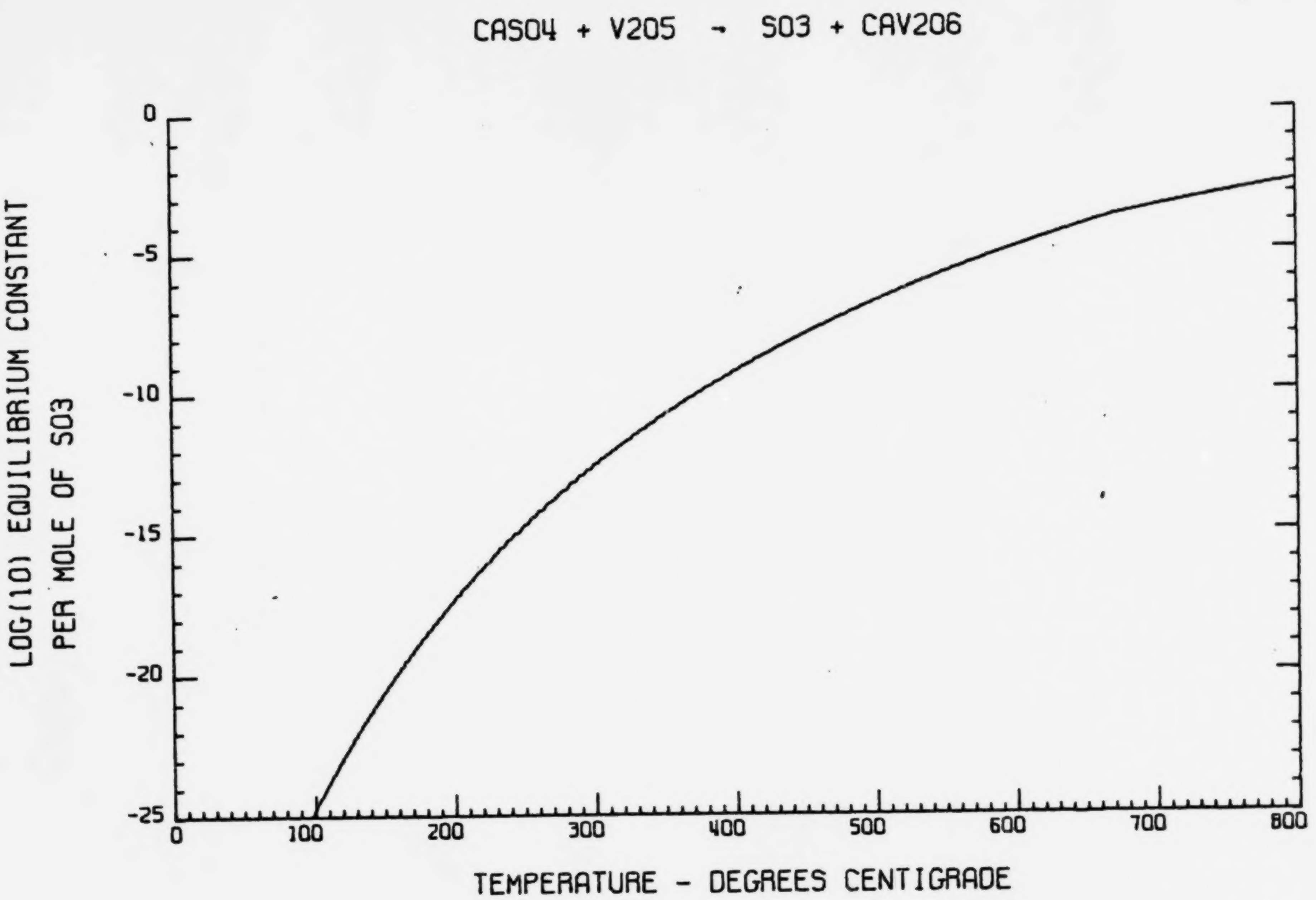


FIGURE 72a Equilibrium between $CaSO_4$ + V_2O_5 and SO_3 + CaV_2O_6

Temp. °C	Gasgeschwindigkeiten pro Minute A. 150 cm³ Ausbeute °/₀	A. 150 cm³ °/₀ der theor. Menge	B. 300 cm³ Ausbeute °/₀	B. 300 cm³ °/₀ der theor. Menge
450	9,3	9,4	—	—
500	15,2	15,8	5,8	6,0
550	20,9	23,1	10,8	11,9
600	24,3	29,8	17,2	21,1
650	26,9	37,0	19,2	27,0
675	25,8	39,4	20,3	31,0
700	24,9	41,8	20,3	35,8

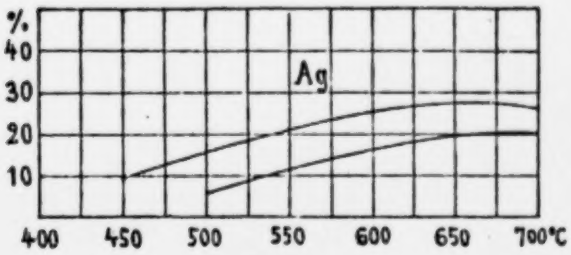


Fig. 7.

Table 26 and Figure 73:

Conversion of SO_2 to SO_3 over Ag on asbestos.

7% SO_2, 19.53% O_2, 73.47% N_2; streaming rate 150 and 300 cm^3/min.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 696-734 (1928).

The conversion of SO_2 to SO_3 over Ag was very poor. After the test, it was found that about 70% of the silver was transformed into Ag_2SO_4. It was suggested that the rest was oxidized to Ag_2O. This was not proven. It is assumed that copper would be a less effective catalyst.

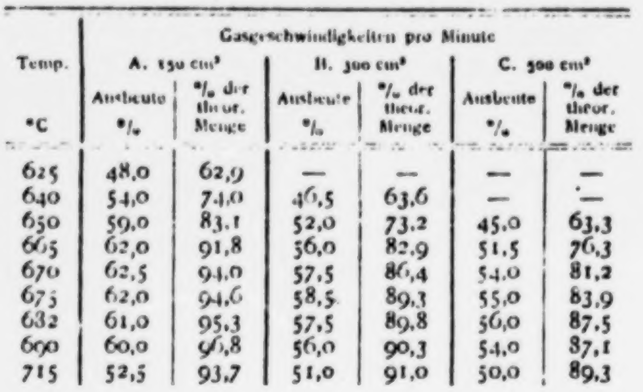
$\underline{WO_3}$ (NE-002)

WO_3 was reported to be effective in combination with V_2O_5 (FI-001). In an English patent it was reported to have good catalytic efficiency when used as a single oxide (FI-002).

Neumann (NE-002) prepared the catalyst in the following way:

15 g of pumice-stone (2-5 mm grain diameter) were mixed with 7.5 g WO_3, moistened, mechanically mixed and dried at 120° C.

The following results were obtained:



Temp.	Gasgeschwindigkeiten pro Minute					
	A. 150 cm^3		II. 300 cm^3		C. 500 cm^3	
°C	Ausbeute °/₀	°/₀ der theor. Menge	Ausbeute °/₀	°/₀ der theor. Menge	Ausbeute °/₀	°/₀ der theor. Menge
625	48,0	62,9	—	—	—	—
640	54,0	74,0	46,5	63,6	—	—
650	59,0	83,1	52,0	73,2	45,0	63,3
665	62,0	91,8	56,0	82,9	51,5	76,3
670	62,5	94,0	57,5	86,4	54,0	81,2
675	62,0	94,6	58,5	89,3	55,0	83,9
632	61,0	95,3	57,5	89,8	56,0	87,5
690	60,0	96,8	56,0	90,3	54,0	87,1
715	52,5	93,7	51,0	91,0	50,0	89,3

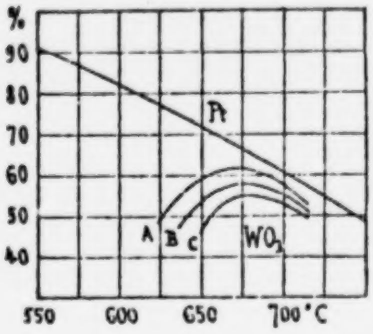


Fig. 6.

B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 695-734 (1928).

Table 27 and Figure 74:

Conversion over WO_3 catalyst; 7% SO_2, 19.53% O_2, 73.47% N_2. Streaming rates 150 ml/min (A), 300 ml/min (B), and 500 ml/min (C).

Conclusions: WO_3 acted as a poor catalyst. The maximum catalytic activity was reached at about 670° C.

Observations: The WO_3 catalyst was yellow at the start but after the experiment was light green. This indicated that a reduction took place.

Iron-Oxide (NE-004)

The efficiency of iron oxide in oxidizing SO_2 to SO_3 was known as early as 1852 (WO-004). It has been used in industrial processes since 1898 (DE-001). Several publications cover this subject (LU-001, LU-002, DA-001, and KE-007). The measured conversions of these investigations as a function of temperature are shown in Figure 75.

Neumann and Goebel prepared the iron oxide in the following way: An iron vitriol solution was oxidized with HNO_3 and the iron precipitated with NH_4OH. The precipitate was washed carefully, dried at 110° C and then heated for a long time (no exact data given) at 300-400° C. The amount of oxide used was 27.5 g, and the length of the fixed bed was 12 cm. The catalyst grain diameter was 3-5 mm.

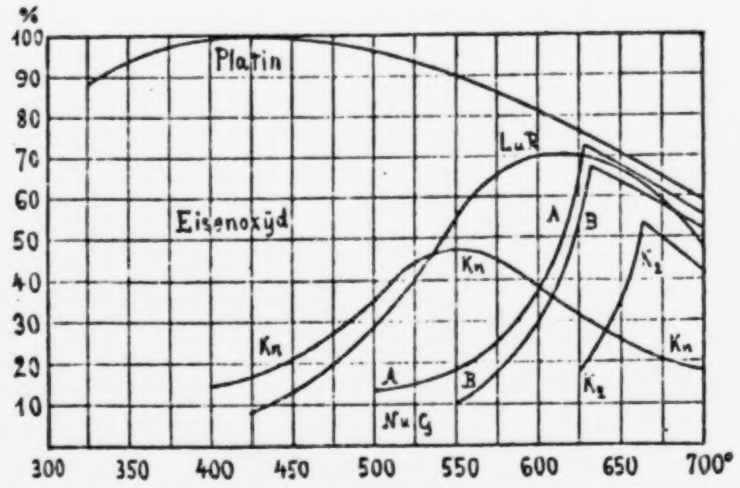


Fig. 8.

FIGURE 75

SO_2 conversion over different iron catalysts; 7% SO_2, 19.53% O_2, 73.47% N_2, Streaming rate: 150 ml/min (A), 300 ml/min (B) for plots A and B. A and B: results from Neumann and Goebel

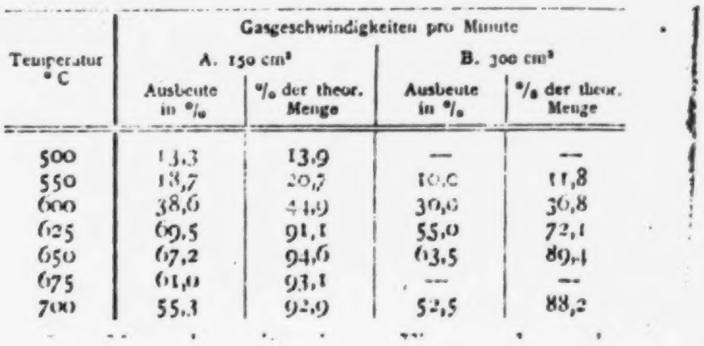
Kn: Results from Knietsch

LuR: Results from Lunge and Reinhardt

K_2: Results of Keppeler

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

The following table shows the results of Neumann and Goebel for flow rates of 150 and 300 ml/min (plots A and B in Figure 75).



Temperatur °C	Gasgeschwindigkeiten pro Minute			
	A. 150 cm^3		B. 300 cm^3	
	Ausbeute in %	% der theor. Menge	Ausbeute in %	% der theor. Menge
500	13,3	13,9	—	—
550	18,7	20,7	10,0	11,8
600	38,6	44,9	30,0	36,8
625	69,5	91,1	55,0	72,1
650	67,2	94,6	63,5	89,4
675	61,0	93,1	—	—
700	55,3	92,9	52,5	88,2

TABLE 28

SO_2 conversion over iron oxide, 7% SO_2, 19.53% O_2, 73.47% N_2, Streaming rate: 150 cm^3/min (A) and 300 cm^3/min (B).

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Figure 76 shows the physical adsorption of SO_2 in ml on 1 g iron oxide (NE-005), as function of temperature up to 400° C. Only small amounts of $FeSO_4$ could be detected in the residues. This result confirms the finding of Hammick (HA-001), who reported that iron oxide was not attacked at all by SO_2 at 450° C and that between 700-800° C only a small amount of reduction took place.

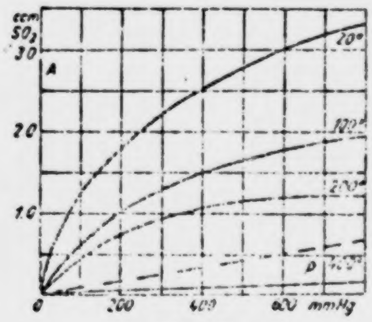


Fig. 9.

FIGURE 76
Adsorption of SO_2 on iron oxide as function of SO_2 pressure and temperature. The scale of the ordinate is adsorbed ml SO_2/g Fe_2O_3.

9. NEUMANN, E. GOEBEL, 'DIE ADSORPTION VON SCHWEFLIGER SAURE AN PLATIN, EISENOXYD UND CHROMOXYD, II.,' Z. ELECTROCHEM., VOL. 30, PP. 672-82 (1933).

The physical adsorption on Cr_2O_3 was higher, see Figure 77 (NE-005). There was no reaction between SO_2 and Cr_2O_3 detected at temperatures up to 400° C.

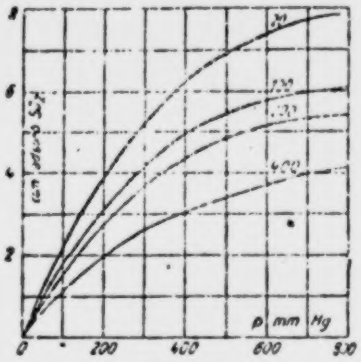


Fig. 16.

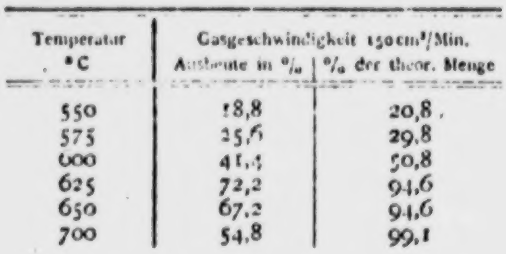
FIGURE 77

Physical Adsorption of SO_2 on Cr_2O_3. The scale of the ordinate is adsorbed ml SO_2/ g Cr_2O_3.

B. NEUMANN, E. GOEBEL, 'DIE ADSORPTION VON SCHWEFLIGER SAURE AN PLATIN, EISENOXYD UND CHROMOXYD, II.,' Z. ELECTROCHEM., VOL. 30, PP. 672-82 (1933).

Fe_2O_3 - Bi_2O_3 (NE-004)

It is known that Bi_2O_3 improves the efficiency of iron oxide contacts in oxidizing NH_3 to nitrogen oxides (BA-003). Neumann and Goebel measured the SO_2 conversion (with a Fe_2O_3 + 4%Bi_2O_3 catalyst). The results are given in Table 29:



Temperatur °C	Gasgeschwindigkeit 150cm³/Min.	
	Ausbeute in %	% der theor. Menge
550	18,8	20,8
575	25,6	29,8
600	41,4	50,8
625	72,2	94,6
650	67,2	94,6
700	54,8	99,1

TABLE 29

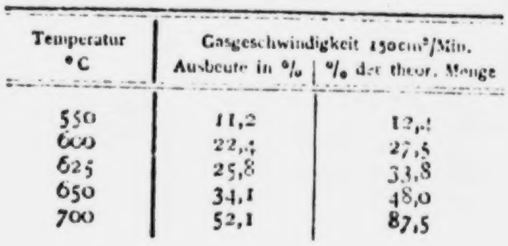
Conversion of SO_2 to SO_3 over Fe_2O_3 + 4% Bi_2O_3, 7% SO_2, 19.53% O_2, 73.47% N_2. Streaming rate: 150 ml/min. (NE-004)
B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Conclusions: The optimum conversion of 94.6% of the theoretical amount was at about 625°C. Pure Fe_2O_3 reacts at the same temperature to give a conversion of about 91.1% of the theoretical amount. Therefore, Fe_2O_3 was activated only in a small degree by Bi_2O_3.

$\underline{Fe_2O_3 - K_2O}$ (NE-004)

With Fe_2O_3 + 40% K_2O, the results shown in Table 30 were obtained (length of fixed bed 12 cm). Figure 78 shows the results in graphical form.

Conclusions: The alkali oxide does not improve the efficiency of Fe_2O_3, on the contrary, it makes the conversion worse.



Temperatur °C	Gasgeschwindigkeit 150cm³/Min. Ausbeute in %	% der theor. Menge
550	11,2	12,4
600	22,4	27,5
625	25,8	33,8
650	34,1	48,0
700	52,1	87,5

TABLE 30

SO_2 conversion over Fe_2O_3 + 40% K_2O. 7% SO_2, 19.53% O_2, 73.47% N_2. Streaming rate: 150 ml/min.

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

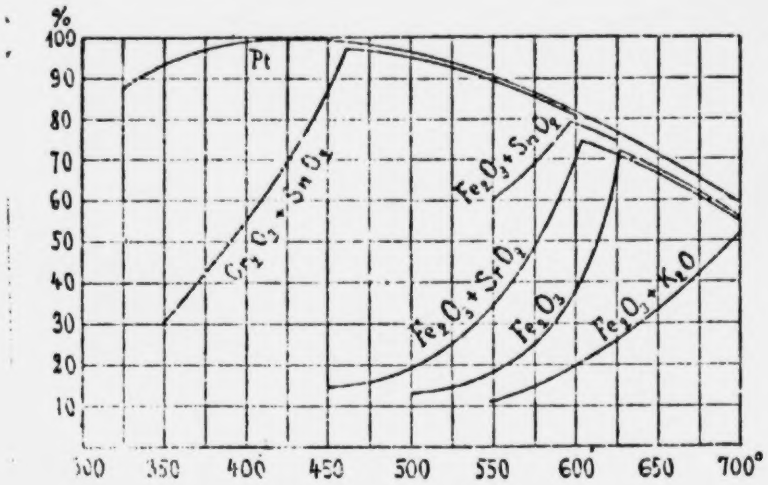


FIGURE 78

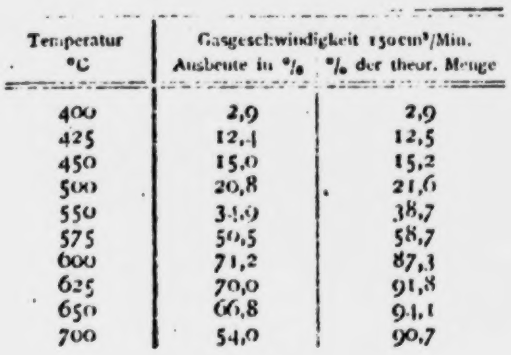
Conversion over different oxide systems, 7% SO_2, 19.53% O_2, 73.47% N_2

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Fe_2O_3-SrO (NE-004)

SrO was reported in 1910 to improve the iron oxide catalyst (AL-001). Neumann and Goebel prepared a catalyst using magnesia as a carrier.

Magnesia was heated with a concentrated solution containing $Fe(NO_3)_3$ and $Sr(NO_3)_2$ in the molar ratio of 1:1½ and then dried. The catalyst mass was heated in an oxygen atmosphere at 500° C until all nitrogen oxides escaped. With 26 g. of the mass in a bed of 12 cm length the following results were obtained (See Table 31 and Figure 78).



Temperatur °C	Gasgeschwindigkeit 150 cm³/Min. Ausbeute in %	% der theor. Menge
400	2,9	2,9
425	12,4	12,5
450	15,0	15,2
500	20,8	21,6
550	34,9	38,7
575	50,5	58,7
600	71,2	87,3
625	70,0	91,8
650	66,8	94,1
700	54,0	90,7

TABLE 31

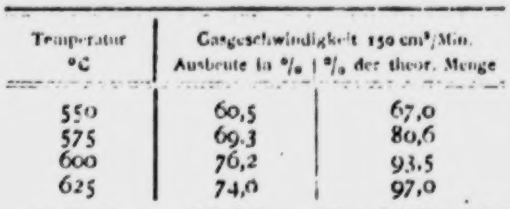
SO_2 conversion over a Fe_2O_3-SrO catalyst; 7% SO_2; 19.53% O_2, 73.47% N_2. Streaming rate: 150 ml/min.

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Conclusions: SrO improves the efficiency of iron oxide. The improvement was lost after several runs. The cause was probably formation of strontium sulfate. This fact was not confirmed by experiments.

Fe_2O_3-SnO_2 (NE-004)

Catalyst preparation: $Fe(OH)_3$ and $Sn(OH)_4$ were precipitated in a 1:1 molar ratio, filtered, and heated to about 600° C. The results shown in Table 32 were obtained (See also Figure 78).



Temperatur °C	Gasgeschwindigkeit 150 cm³/Min.	
	Ausbeute in %	% der theor. Menge
550	60,5	67,0
575	69,3	80,6
600	76,2	93,5
625	74,0	97,0

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

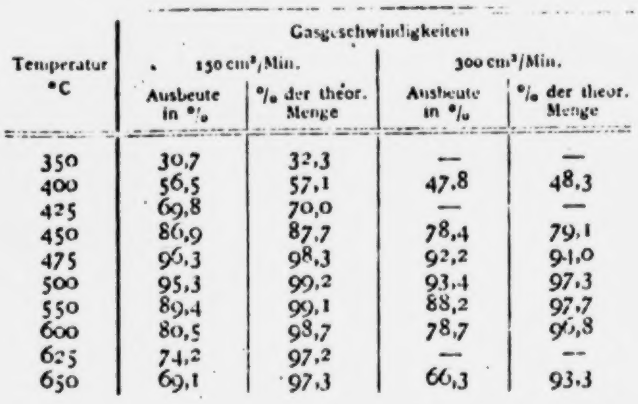
TABLE 32

SO_2 conversion over Fe_2O_3-SnO_2. 7% SO_2, 19.53% O_2, 73.47% N_2; Streaming rate: 150 ml/min.

Conclusions: SnO_2 improves the efficiency of Fe_2O_3 remarkably.

Cr_2O_3-SnO_2 (NE-004)

Catalyst preparation: $Cr_2(SO_4)_3$ was precipitated with NH_4OH. $Sn(OH)_4$ was prepared separately. Both hydroxides were mixed in a molar ratio 1:1 and calcined at about 700° C. The following table and Figure 78 show the conversion obtained.



Temperatur °C	Gasgeschwindigkeiten 150 cm³/Min. Ausbeute in %	150 cm³/Min. % der theor. Menge	300 cm³/Min. Ausbeute in %	300 cm³/Min. % der theor. Menge
350	30,7	32,3	—	—
400	56,5	57,1	47,8	48,3
425	69,8	70,0	—	—
450	86,9	87,7	78,4	79,1
475	96,3	98,3	92,2	94,0
500	95,3	99,2	93,4	97,3
550	89,4	99,1	88,2	97,7
600	80,5	98,7	78,7	96,8
625	74,2	97,2	—	—
650	69,1	97,3	66,3	93,3

TABLE 33

SO_2 conversion over $Cr_2O_3 + SnO_2$; 7% SO_2, 19.53% O_2, 73.47% N_2; Streaming rates 150 and 300 ml/min.

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Conclusions: The conversion reached 98.3% of the theoretical amount at 475° C and 99.2 % at 500° C. The plot in Figure 78 shows that the conversion was also very high in the 350-400° C region. SnO_2 causes marked improvement in the efficiency of Cr_2O_3.

$\underline{SnO_2}$ (NE-004)

Catalyst preparation: $Sn(OH)_4$ was precipitated from a $SnCl_4$ solution with NH_4OH, washed and heated in air. The following results were obtained:

Temperatur °C	Gasgeschwindigkeit 150 cm³/Min. Ausbeute in %	% der theor. Menge
400	0,0	0,0
500	4,9	5,1
600	13,4	16,4
700	25,2	41,6
725	29,2	54,6
750	35,2	73,7

TABLE 34

SO_2 conversion over SnO_2; 7% SO_2, 19.53% O_2, 73.47% N_2;

Streaming Rate: 150 cm^3/min.

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Conclusions: The efficiency of SnO_2 was very poor.

Observations: At the end of the tests most of the catalyst still consisted of tin oxide. However, small amounts of $SnSO_4$ and $Sn(SO_4)_2$ were found. The results are shown in a graphical form in Figure 79.

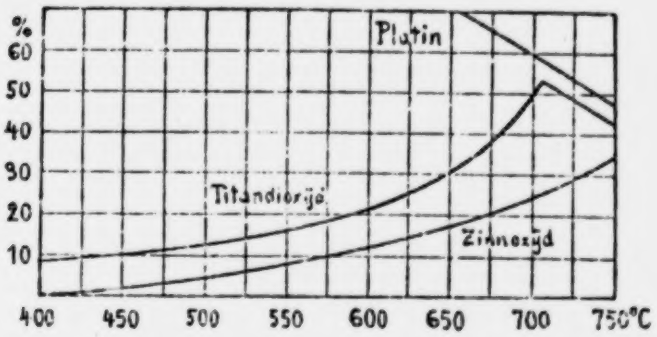


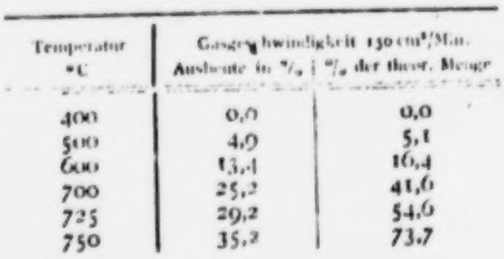
FIGURE 79

SO_2 conversion over TiO_2 and SnO_2; Streaming Rate: 150 ml/min.

B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

TiO_2 (NE-004)

Catalyst Preparation: $Ti(OH)_4$ was heated to about 500° C (exact temperature was not given). The following results were obtained:



Temperatur °C	Gasgeschwindigkeit 130 cm³/Min.	
	Ausbeute in %	% der theor. Menge
400	0,0	0,0
500	4,9	5,1
600	13,4	16,4
700	25,2	41,6
725	29,2	54,6
750	35,2	73,7

TABLE 35

SO_2 conversion over TiO_2; 7% SO_2, 19.53% O_2, 73.47 N_2

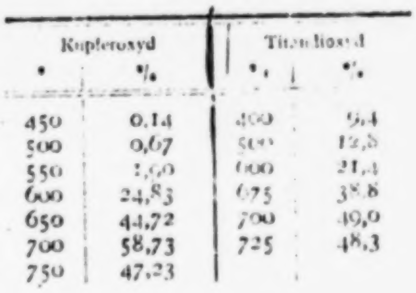
B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

Conclusions: The results were more favorable than those for SnO_2, but much worse than the conversion reached with Fe_2O_3.

Observations: After the tests, most of the catalyst still consisted of TiO_2, however $TiOSO_4$ was also detected. Part of the glass contact tube turned blue during the experiment. This indicated that traces of the TiO_2 were reduced to Ti^{+++}. It was concluded, that TiO_2 was therefore a bad catalyst, because the reduction step, $TiO_2 \rightarrow Ti_2O_3$, goes too slowly.

CuO (NE-006)

Catalyst Preparation: Pure CuO was moistened, formed into tablets, and calcined at 400° C. The conversion is compared in Table 35 with that over TiO_2.



Kupferoxyd		Titandioxyd	
°	%	°	%
450	0,14	400	9,4
500	0,67	500	12,5
550	1,60	600	21,4
600	24,83	675	38,8
650	44,72	700	49,0
700	58,73	725	48,3
750	47,23		

TABLE 35

Conversion of SO_2 over CuO and TiO_2; 7% SO_2, 19.53% O_2, 73.47% N_2

B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

The following mechanism was proposed.

$$2\ CuO + SO_2 \rightarrow Cu_2O \cdot SO_3 \qquad (76a)$$

$$Cu_2SO_4 \rightarrow Cu_2O + SO_3 \qquad (76b)$$

$$Cu_2O + \tfrac{1}{2}\ O_2 \rightarrow 2\ CuO \qquad (76c)$$

The catalyst became more and more inactive at temperatures lower than 650 due to the formation of $CuSO_4$. The results are given in Figure 80 in graphical form.

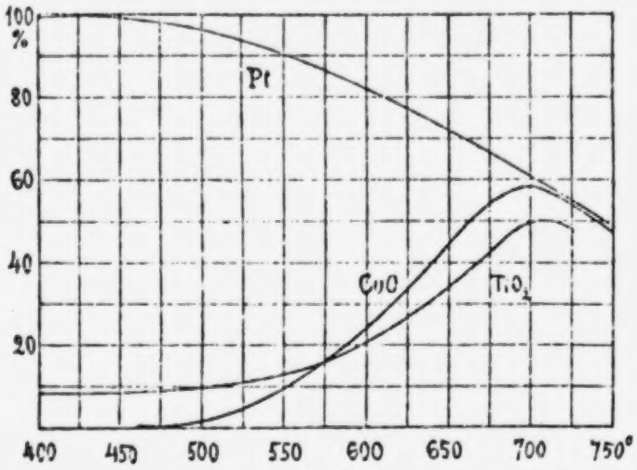


Fig. 2.
Umsatz mit CuO und TiO_2.

B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

FIGURE 80

SO_2 conversion over CuO and TiO_2; 7% SO_2, 19.53% O_2, 73.47% N_2, The streaming rate was not given, probably 150 cm^3/min.

$\underline{MnO_2}$ (NE-006)

Catalyst Preparation: A permanganate solution was reduced with alcohol. The hydrated MnO_2 was dried at 300° C. The catalyst was treated for several hours at 550-650° C with a 7% SO_2-air mixture. The following results were obtained.

TEMPERATURE °C	CONVERSION PERCENT
450°	2,94%
500	8,47
550	18,33
600	11,98
650	15,68
700	22,03

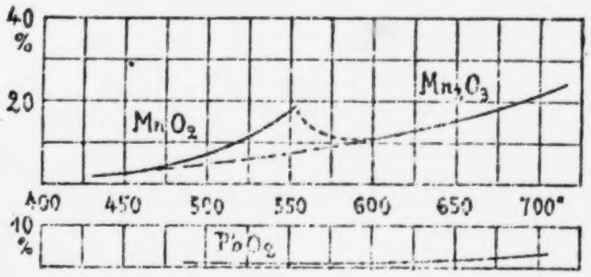


Fig. 4.
Umsatz mit MnO_2 und PbO_2.

TABLE 35 and FIGURE 81 - Conversion over MnO_2 and PbO_2 Catalysts

B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

It was reported that MnO_2 was transformed at 530° C to Mn_2O_3 (SI-002) and at 940° C to Mn_3O_4 (ME-002). The dissociation pressure for the reaction $2MnO_2 \rightleftharpoons Mn_2O_3 + \frac{1}{2}O_2$, as measured by Askenasy and Klonows (AS-001), is as follows:

°C	mm Hg
382	23
448	125
478	200
536	>1040

Thermodynamic computations by TRACOR (T.M. 004-009-Ch7) yielded a partial pressure of O_2 of 21 mm Hg at 390° C for MnO_2. This agrees well with Askenasy and Klonows (AS-001).

MnO_2 was effective as a catalyst as long as it was not transformed totally into Mn_2O_3. The reverse reaction is not possible in air because at temperatures of about 450° C, the dissociation pressure of MnO_2 becomes greater than the O_2 partial pressure in air. Over 550° only Mn_2O_3 was effective. Mn_2O_3 was finally transformed into $MnSO_4$. Mn_3O_4 was reported to have the same efficiency as Mn_2O_3 in the range from 500 to 700° C.

$\underline{PbO_2}$ (NE-006)

Balarew (BA-004) reported that the O_2 pressure for the reaction:

$$3PbO_2 \rightleftharpoons Pb_3O_4 + O_2 \qquad (77)$$

reached one atmosphere at 340° C. At about 575° C, Pb_3O_4 and Pb_2O_3 decomposed to PbO. PbO_2 was transformed totally into $PbSO_4$ during catalysis. The catalyst then became inactive. The conversions obtained with PbO_2 are shown in Figure 81.

$\underline{MoO_3}$ (NE-006)

Catalyst Preparation: $(NH_4)_2\ MoO_4$ was heated to 400° C.

MoO_3 began to sublime at about 600° C (GM-001). The conversions with the 7% SO_2-air mixture are given in Table 36 and Figure 82.

500°	0,29%
550	1,43
600	2,85
650	34,61
700	45,76
750	43,78

TABLE 36

SO_2 conversion over MoO_3

B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

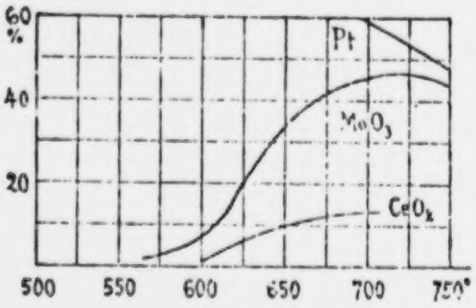


Fig. 5.

FIGURE 82

SO_2 conversion over MoO_3 and CeO_2; 7% SO_2, 19.53 O_2, 73.47% N_2

B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 33, PP. 304-11 (1932).

It was reported that the catalyst mass changed during the experiment. There were no details given.

Bi_2O_3 (NE-006)

This element showed poor catalytic behavior. At temperatures above 600° C SO_3 vapor developed. Neumann reported that this was presumably due to the decomposition of a sulfate formed at lower temperatures.

UO_3 (NE-006)

UO_3 was heated with a 7% SO_2-air mixture. At about 700° C evolution of SO_3 vapor occurred. The UO_3 was transformed into U_3O_8. Biltz and Müller (BI-005) reported that this transformation occurred at temperatures above 400° C. U_3O_8 was then stable up to 750° C, at which temperature more oxygen was lost. After the test, part of the catalyst was found to consist of UO_2SO_4. Thermodynamic calculations by TRACOR indicated that the conversion of UO_3 to U_3O_8 should take place at 544° C at an O_2 partial pressure of 21 mm Hg.

$\underline{CeO_2}$ (NE-006)

The conversion using CeO_2 powder was as follows:

TEMPERATURE °C	CONVERSION PERCENT
600°	1,83%
650	9,49
700	13,67

After the test cerium sulfate was found in the catalyst mass.

V. CORRELATION OF DATA - SELECTION OF POTENTIAL SORBENTS

Information on the physical and chemical properties of the sulfites, the decomposition behavior of the sulfates, the catalytic behavior of the oxides, and the price of each species is summarized in Table 37.

Most of the data for the possible sorption range with sulfite formation and the sulfite decomposition temperatures are based on thermodynamic calculations. Along with the thermodynamically predicted disproportionation behavior, we have included experimental descriptions of disproportionation conditions taken from the open literature. The sulfate decomposition data were taken from T.M. 004-009-Ch8, and the prices from T.M. 004-009-Ch6. The description of catalytic behavior is based on Part IV of this memorandum as well as on the idea that a change in oxidation state must be possible for an oxide in order for it to be catalytically effective.

We have used the "Remarks" column to make a statement about the applicability of the particular oxide to the sorption of SO_2. We have based our recommendation on the following things:

1) Disproportionation behavior of the sulfite
2) Thermodynamically predicted sorption behavior with formation of sulfite.
3) Sulfate decomposition temperature
4) Price of the metal, oxide, or salt.
5) Catalytic activity of the oxide

TABLE 37

PROPERTIES OF OXIDES, SULFATES, AND SULFITES

OXIDE	POSSIBLE SORPTION* RANGE WITH SULFITE FORMATION	DISPROPORTIONATION* RANGE OF SULFITE	DECOMPOSITION* TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
1) Li_2O	25 to 800° C	Thermodynamically favored between 25-800° C. Rate becomes appreciable at 650° C.	> 800° C	> 860° C (melting point)	Inactive	Metal: 15,000 Carbonate: 850 Sulfite: 2,400	Not a potential sorbent. 1) Sulfite disproportionates. 2) Sulfate decomposition temperature is too high.
2) Na_2O	25 to 800° C	Thermodynamically favored between 25-800° C. Rate becomes appreciable at 600° C.	> 800° C	> 900° C Weight loss when held for 2 hrs. at 1200° C is 1.05%.	Inactive	Metal: 400 Carbonate: 30 Sulfate: 20	Not a potential sorbent. 1) Sulfite disproportionates. 2) Sulfate decomposition temperature is too high
3) K_2O	25 to 800° C	Thermodynamically favored between 25-800° C. Rate becomes appreciable at temperatures above 750° C.	> 800° C	> 900° C. Weight loss when held for 2 hrs. at 1200° C is 3.6%.	Inactive	Salts: 20	Not a potential sorbent. 1) Sulfite disproportionates. 2) Decomposition temperature of sulfate is too high.
4) Rb_2O	Unknown	Unknown	Unknown	> 900° C. Weight loss when held for 2 hrs. at 1200° is 6.3%.	Inactive	Metal: 1.5 million Carbonate: 280,000	Not a potential sorbent. 1) Too expensive. 2) The sulfite will probably disproportionate. 3) The decomposition temp. of the sulfate is too high.
5) Cs_2O	Unknown	Unknown	Unknown	> 1036° C. Weight loss when held for 2 hrs. at 1200° C is 13.9%.	Inactive	Metal: 400,000 Carbonate: 64,000	Not a potential sorbent. 1) Too expensive. 2) Sulfite probably disproportionates. 3) The decomposition temperature is too high for the sulfate.
6) BeO	Sorption not possible at temp. greater than 25° C.	Shows no tendency to disproportionate thermodynamically.	150° C	690 to 760° C	Inactive	Metal: 130,000 Beryl(11% BeO): Buyer-Seller Basis	Not a potential sorbent. 1) Poisonous 2) Sulfite decomposition temp. too low. 3) Oxide is inactive, sorption with sulfate formation would be slow.
7) MgO	Possible at temp. less than 150° C	Thermodynamically favored between 25-800° C. The amount of sulfite converted to sulfite is 5-18% between 300 and 600° C.	350° C	Static method- ≥ 950° C Dynamic method- ≥ 871° C	Inactive	Metal: 705 Carbonate: 285	Not a potential sorbent. 1) Percent disproportionation is small but important. 2) Sulfate decomposition temperature is too high.

* Thermodynamic calculations were made only in the temperature range from 25 to 800° C.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION* RANGE WITH SULFITE FORMATION	DISPROPORTIONATION* RANGE OF SULFITE	DECOMPOSITION* TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
8) CaO	< 590°C	Thermodynamic tendency to disproportionate from 25 to 800°C. Rate becomes appreciable at 600°C.	> 800°C	> 1227-1527°C	Inactive CaO_2: possibly high oxidation power(see Fig.65)	Metal: 4,000	Not a potential sorbent. 1) Sulfite decomposition temp. too high. 2) Disproportionation of sulfite. 3) Sulfate decomposition temp. too high.
9) SrO	25 to 800°C	Thermodynamic tendency to disproportionate from 25 to 800°C. Rate becomes appreciable at 450°C.	> 800°C	1374°C	Inactive	Sulfate: 60 Carbonate: 400-700	Not a potential sorbent. 1) Sulfate decomposition temp. too high. 2) Sulfite disproportionates. 3) Sulfite decomposition temp. is too high.
10) BaO	25 to 800°C	Thermodynamic tendency to disproportionate from 25 to 800°C. Rate becomes appreciable at 500°C.	> 800°C	> 1347 (m.pt.)	Inactive BaO_2: possibly high oxidation power(see Fig.65)	Oxide: 288 Sulfate: 20 Carbonate: 112	Not a potential sorbent. 1) Sulfite disproportionates. 2) Sulfate decomposition temperature too high. 3) Sulfite decomposition temperature too high.
11) Sc_2O_3	Unknown	Found by experiment to disproportionate from 300 to 550°C. Secondary reactions with sulfur formation at 300°C.	Decomposition should be appreciable at the same temp. as disproportionation.	780°C	Probably inactive	Oxide: 3,500,000 to 5,200,000	Not a potential sorbent. 1) Too expensive.
12) Y_2O_3	Unknown	Found by experiment to disproportionate from 500 to 800°C. Secondary reactions with sulfur formation at 700°C.	Decomposition should occur and compete with disproportionation.	1124°C. Before decomposition a basic sulfate is formed.*	Probably inactive	Metal: 500,000 to 1,000,000	Not a potential sorbent. 1) Too expensive. 2) Sulfite disproportionates. 3) Sulfate decomposition temperature too high.
13) La_2O_3	Unknown	Found experimentally to disproportionate appreciably from 400 to 700°C. Secondary reactions with sulfur formation at 650°C.	Decomposition and disproportionation are are competing reactions.	> 1096°C Basic sulfate is formed before decomposition.	Probably inactive		Not a potential sorbent. 1) Probably too expensive. 2) Sulfite disproportionates. 3) Sulfate decomposition temp. too high.
14) Ce_2O_3	Unknown	Decomposition and disproportionation are expected on the basis of similarity to lanthanum and samarium.		> 650°C Decomposition product is CeO_2.	Probably active	Metal: 150,000	Potential sorbent 1) Sulfate decomposition is not too high. 2) Shows catalytic activity.
CeO_2	Unknown	Unknown	Unknown	> 860°C	1.8-13.7% conversion of SO_2 from 600 to 700°C. Some sulfate found in catalyst mass.	Oxide: 8,000	Potential sorbent 1) Sulfate decomposition is not too high. 2) Shows catalytic activity.

* Thermodynamic calculations were made only in the temperature range from 25 to 800°C.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION RANGE WITH SULFITE FORMATION	DISPROPORTIONATION RANGE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
15) TiO_2	Unknown	Unknown	Unknown	430 to 600° C Basic sulfate is formed before decomposition.	Poor since reaction Ti_2O_3-TiO_2 goes too slowly.	Oxide: 120	Potential sorbent: 1) Sulfate dec position temp. seems favorable for sorption. 2) TiO_2 reacts too slowly. In catalytic experiments only small amounts of $TiOSO_4$ were found.
16) ZrO_2	Possible at temperatures below 330° C.	Unknown	600° C[1]	576 to 632° C[1] Basic sulfate formed before decomposition.	Probably inactive	Metal: 10,500 to 36,000 Oxide: 600 to 3,000	Potential sorbent 1) Sulfate decomposition temp. is favorable. 2) Oxidation power can be expected to be very low.
17) HfO_2	Unknown	Unknown	Unknown	550 to 650° C	Probably inactive	Metal: 150,000 to 276,000	Same as for ZrO_2
18) V_2O_3	Unknown	Unknown	Unknown	> 400° C Decomposition product is mixture of V_2O_4 and V_2O_5	Good catalyst. Conversion takes place from 400-700° C. Part of V_2O_5 is reduced.	V_2O_5 2,400 to 2,600	Potential sorbent: 1) Kinetics of reaction below 400° C discouraging. 2) Thermodynamically favorable.
VO_2	Unknown	Unknown	Unknown				
V_2O_5	Unknown	Unknown	Unknown				
19) Nb_2O_5	Unknown	Unknown	Unknown	Unknown	Unknown	Oxide containing ore: 2,000 to 8,000 Metal: 20,000 to 60,000	Insufficient information for decision.
20) Ta_2O_5	Unknown	Unknown	Unknown	Unknown	Unknown	Pentoxide: 15,000 to 16,000	Insufficient information for a decision.
21) Cr_2O_3	Unknown	Unknown	Unknown	Decomposition to basic sulfate 460-640°C. Sulfate decomposition temp. unknown.	SO_2 physically adsorbed on Cr_2O_3, no reaction to 400° C. Efficiency of Cr_2O_3-SnO_2 mixture is very high from 350 to 400° C.	Ore(50% Cr_2O_3): 18 to 36	Potential sorbent: 1) sulfate decomposition temperature probably favorable. 2) the reactivity with SO_2 up to 400° C is very poor.

---

[1] There seems to be a discrepancy between theoretical and experimental results. If sulfate decomposes at 576 to 632° C, the sulfite should decompose at much lower temperatures.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION RANGE WITH SULFITE FORMATION	DISPROPORTIONATION RANGE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
22) MoO_3	Unknown	Unknown	Unknown	Unknown	MoO_3 catalyst converts 45% SO_2 from 500-700° C. Catalyst mass undergoes undescribed change.	Metal: 3,200 Oxide: 2,800	Not a potential sorbent. Sublimes rapidly at 600° C.
23) WO_3	Unknown	Unknown	Unknown	Unknown	Poor: Conversion reaches a maximum of 62% at 675° C. Catalyst is partly reduced.	Metal: 35-45	No decision possible.
24) MnO	< 240° C	Thermodynamic tendency to disproportionate from 25 to 800° C	440° C	$MnSO_4$ is oxidized in O_2 containing atmosphere. Decomposition between 1090-1100° C.	Poor catalytic activity. Catalyst mass is transformed to $MnSO_4$	Metal: 590	Not a possible sorbent. 1) Shows excellent sorption behavior (especially MnO_2) with $MnSO_4$ formation. 2) Decomposition temperature of sulfate is too high. 3) Active form of sorbent difficult to regenerate.
Mn_2O_3	< 20° C	---------	130° C	1090-1100° C	Same as MnO.	Same as MnO.	Same as MnO.
MnO_2	Sorbs with formation of sulfate.	---------	-----	1090-1100° C for $MnSO_4$.	Same as MnO.	Same as MnO.	Same as MnO.
25) ReO_2	Unknown	Unknown	Unknown	Unknwon	Unknown	Metal: 1,160,000	Not a possible sorbent. 1) Too expensive.
26) FeO	< 190° C	Thermodynamic tendency to disproportionate from 25-800° C.	380° C	Oxidation takes place at 520-530° C.	Good (used as commercial catalyst)	Ore: 8.5 Oxide Pigments: 60-440	Potential sorbent: 1) Thermodynamically favorable. 2) Kinetics of the reaction below 400° C discouraging.
Fe_2O_3	Sulfite is unstable at temperatures above 60° C.	-------	60° C	Literature disagreement, probably 650° C.	Same as FeO.	Same as FeO.	Same as FeO.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION RANGE WITH SULFITE FORMATION	DISPROPORTIONATION RANGE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
27) CoO	< 250° C	Thermodynamically favored from 25 to 800° C.	470° C	800-1000° C End product is Co_3O_4	No data.	Metal: 3,000-3,300 Oxide: No data.	Potential sorbent: 1) Co_xO_y can be expected to have a good oxidation power (See Figure 65). 2) Decomposition temperature of sulfate is a little too high.
28) NiO	< 180° C	Thermodynamically favored between 25 and 800° C.	410° C	About 800° C	Unknown	Metal: 1,900 Oxide: 1,800	Potential sorbent: 1) The higher oxides, Ni_xO_y, can be expected to have a high enough oxidation power for SO_2 oxidation. 2) Sulfate decomposition temperature is reasonable.
29) Rh_xO_y	Unknown	Unknown	Unknown	Unknown	Unknown	Metal: 1,200,000	Not a potential sorbent: 1) U.S. production 2 tons/yr. 2) Too expensive.
30) IrO_2	Unknown	Unknown	Unknown	Unknown	Unknown	Metal: 4,958,000 to 5,542,000	Not a potential sorbent, too expensive.
31) PdO	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	No decision possible, but probably too expensive.
32) CuO	Sulfite is unstable at temperatures higher than 110° C.	Thermodynamically favored from 25 to 800° C.	110° C	840-935° C	Poor, (sulfate formation).	Metal: 680 to 760	Potential sorbent: 1) Oxidation power may be high enough. 2) Decomposition temperature of sulfate is not too high.
Cu_2O	Sulfite is unstable at temperatures higher than 100° C.	Thermodynamically favored from 25 to 800° C.	100° C	Cu_2SO_4 is oxidized in air. Decomposes at 840-935° C.	Poor, (sulfate formation).	Same as CuO.	Same as CuO.
33) Ag_2O	< 310° C, Ag_2O is stable to 250° C.	Thermodynamically favored between 25 and 800° C.	Predicted to be > 570° C. The reaction, $2Ag_2SO_3 = 2Ag + SO_2 + Ag_2SO_4$, occurs at 100° C.	> 840° C Decomposition product is metal.	Poor, (sulfate formation).	Metal: 38,000 to 52,000	Not a potential sorbent, sulfate decomposes to metal.
34) ZnO	< 110° C	Thermodynamically favored between 25 and 800° C.	290° C	> 740° C Decomposition goes via oxisulfate as intermediate.	Inactive	Metal: 240-280 Oxide 300-355	Potential sorbent: 1) Disproportionation is 3% at 350° C. 2) Decomposition temperature of sulfate is low enough.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION RANGE WITH SULFITE FORMATION	DISPROPORTIONATION RANGE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
35) CdO	< 230° C	Thermodynamically favored between 25 and 800° C.	450° C	> 1065° C A basic sulfate is formed before decomposition.	Inactive	Metal: 5,160	Not a potential sorbent. 1) Since the decomposition temperature of the sulfite is higher than that for Zn disproportionation will be more extensive. 2) The resulting sulfate cannot be thermally regenerated.
36) B_xO_y	No salts are known to exist.					Element: 7,330	Not a potential sorbent.
37) Al_2O_3	Sulfite is unstable at temperatures above 70° C.	No tendency to disproportionate.	Theoretically 70° C. Literature reports 200 to 300° C.	650-950° C	Inactive	Sulfite: 44 to 76 Oxide 15 to 32	Potential sorbent: 1) Disagreement between estimated and reported decomposition temperature of sulfite. 2) No disproportionation predicted. 3) Sulfate decomposition temperature low enough.
38) Ga_2O_3	Unknown	Unknown	Unknown	Unknown	Unknown	Metal: 860,000 to 1,270,000 U.S. production: 1.12 short tons/yr.	Not a potential sorbent. 1) Price is too high. 2) Production too low.
39) SiO_2	No salts are known to exist.	-----	-----	------	-----	------	Not a potential sorbent.
40) GeO_2	Unknown	Unknown	Unknown	Unknown	Unknown	Oxide: 137,000	Not feasible, U.S. prod. 1.5 tons/yr.
41) SnO_2	Thermodynamically unstable between 25 and 800° C.	------	------	About 600° C.	Poor	Metal: 3,060	Potential sorbent: The poor oxidation power will most probably yield a very low reaction rate.
42) PbO	< 330° C	Tends to disproportionate in the entire temp. range. Rate becomes appreciable at temp. above 300° C.	> 600° C	> 800° C	Poor: It was reported that nearly all oxides(starting with PbO_2) form sulfates.	Metal: 280	Not a potential sorbent. 1) The lead oxides Pb_xO_y, especially PbO_2, show good sorption behavior. 2) Resulting sulfate cannot be thermally regenerated. 3) Poisonous.
43) As_2O_3	No salts are known.	------	-------	-------	-------	----------	Not a potential sorbent, too poisonous.
44) Sb_2O_3	Sulfite is unstable in entire temp. range.	------	-------	Unknown	Unknown	Oxide: 950 to 1,200	No decision possible. According to Fig. 65, the system Sb_2O_5/Sb_6O_{13} has a high oxidation power.

TABLE 37 (continued)

OXIDE	POSSIBLE SORPTION RANGE WITH SULFITE FORMATION	DISPROPORTION-ATION RANGE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFITE	DECOMPOSITION TEMPERATURE OF SULFATE	CATALYTIC BEHAVIOR OF OXIDE	PRICE DOLLARS/SHORT TON	REMARKS
45) Bi_2O_3	< 150° C	Thermodynamically favored in the entire temp. range.	310° C	≈ 860° C Basic sulfate is formed before decomposition.	Unknown	Element (refined): 6,860	Potential sorbent.
46) UO_2	< 130° C	No tendency to disproportionate.	320° C	≥ 500° C Forms basic sulfate before decomposition.	Poor, due to sulfate formation.	U_3O_8: 12,000	Potential sorbent, will sorb SO_2 probably with UO_2SO_4 formation.
47) ThO_2	< 190° C	No tendency to disproportionate.	390° C	> 800° C	Unknown	Metal Pellets: 30,000 Oxide: 12,000 to 20,000	Potential sorbent.

Based on the above criteria, the single metal oxides were divided into three groups: unpotential sorbents, potential sorbents, and oxide lacking sufficient data to classify. These are listed in Table 38, 39, and 40 respectively.

TABLE 38

UNPOTENTIAL METAL OXIDE SORBENTS

lithium
sodium
potassium
rubidium
cesium
beryllium
magnesium
calcium
strontium
barium
scandium
yttrium
lanthanum
molybdenum
manganese
rhenium
rhodium
iridium
palladium
silver
cadmium
boron
gallium
silicon
germanium
lead
arsenic

TABLE 39

POTENTIAL METAL OXIDE SORBENTS

cerium
titanium
zirconium
hafnium
chromium
cobalt
nickel
iron
copper
zinc
aluminum
tin
bismuth
uranium
thorium
vanadium

TABLE 40

METAL OXIDES LACKING SUFFICIENT DATA FOR CLASSIFICATION

niobium
tungsten
antimony
tantalum

The list of potential sorbents may be further screened when kinetic data become available.

BIBLIOGRAPHY

AL-001 ALBERT AND SCHULZ, DEUTSCHES REICHS PATENT 238361 (1910).

AS-001 ASKENASY AND KLONOWSKY, Z. ELEKTROCHEM., VOL. 16, P. 104 (1910).

BA-002 BADISCHE ANILIN UND SODA FABRIK, DEUTSCHES REICHS PATENT 231792.

BA-003 BADISCHE ANILIN UND SODA FABRIK, DEUTSCHES REICHS PATENT 283224

BA-004 D. BALAREW, Z. ANORG. ALLGEM. CHEM., VOL. 134, P. 77 (1914).

BE-001 F. BENTON, J. AM. CHEM. SOC., VOL. 45, P.900 (1923).

BI-004 W. BILTZ, H. MULLER, Z. ANORG. ALLGEM. CHEM., VOL. 163, P. 257 (1927).

BI-005 W. BILTZ, H. MULLER, Z. ANORG. ALLGEM. CHEM., VOL. 163, P.295 (1927).

CL-001 A. CLERICI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI SCANDIO, ITTRIO, LANTANIO, NEODIMIO, SAMARIO,' GAZZ. CHIM. ITAL., VOL. 93, PP. 1444-54 (1963).

CO-003 M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI LANTANIO E SAMARIO,' GAZZ. CHIM. ITAL., VOL. 92, PP.447-53(1962).

CO-004 M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

CO-005 M. COLA, C. CASTELLANI BISI, S. TARANTINO, GAZZ. CHIM. ITAL., VOL. 91, P. 105 (1961).

DA-001 D'ANS, DISSERTATION DARMSTADT, P. 48 (1905).

DE-001 DEUTSCHES REICHS PATENTS 106715, 107995, 108445, 108446.

DE-002 DEUTSCHES REICHS PATENT 310070.

DE-003 DEUTSCHES REICHS PATENT 297922.

BIBLIOGRAPHY (CONTINUED)

DE-004	DEUTSCHES REICHS PATENT 339611.
DE-005	DEUTSCHES RETCHS PATENT 347694.
DI-001	P. V. DIBINA, 'THERMAL STABILITY OF ALUMINUM SULFITES,' KHIM. AND KHIM. TEKH., NO. 5, PP. 902-7 (1960).
ER-003	E. ERDOS, 'EQUILIBRIA IN THE SYSTEMS SO2-CO2-MO,' COLL. CZECH. CHEM. COMMUN., VOL. 27, P. 2152-67 (1962).
EU-001	A. EUCKEN, LEHRBUCH DER CHEM. PHYS., LEIPZIG,(1930),P.627.
FA-001	FARBENFABRIKEN FR. BAYER AND CO., DEUTSCHES REICHS PATENT 280960, 1912
FI-001	FIRMA DE HAEN, DEUTSCHES REICHS PATENT 128616 (1900).
FI-002	FIRMA PINTSCH, ENGLISH PATENT 5026 (1912).
FO-001	F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 179, PP. 261-92 (1924).
FR-002	J. FRAZER, 'MANGANESE DIOXIDE IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE,' J. AM. CHEM. SOC., VOL. 45, P.2841(1923).
FR-003	J. FRAZER, 'THE CATALYTIC OXIDATION OF CARBON MONOXIDE,' J. PHYS. CHEM., VOL. 35, P. 405 (1931).
GA-001	E. ROS. GARRINI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO,E AMMONIO,' GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).
GM-001	L. GMELIN, GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE, SULFUR, PART A PP. 324-51 (1953).
GO-002	M. GOLDSCHMIDT, L. THOMASSEN, VID. SELSKP. SKR. I, MATH. NAT. KLASSE, NO. 2, (1923).

BIBLIOGRAPHY (CONTINUED)

HA-001 HAMMICK, J. CHEM. SOC. , III, P. 331, (1917).

HO-001 H. N. HOLMES. A. L. ELDER, IND. ENG. CHEM., VOL. 22, P. 471 (1930).

HU-003 HUTTIG AND SCHRODER, Z. ANORG. ALLGEM. CHEM., VOL. 121, P.243 (1922).

KE-005 A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

KE-007 KEPPELER, Z. ANGEW. CHEM., VOL. 21, PP. 552-77 (1908).

KR-003 C. KROGER, 'ZUR HETEROGENEN KATALYSE BINARER GASREAKTIONEN,' Z. ANORG. CHEM., VOL. 205, PP. 369-97 (1932).

KU-005 KUHLMANN, DEUTSCHES REICHS PATENT 406864.

LE-001 LE BLANC, E. MOBIUS, Z. PHYS. CHEM., VOL. 142, P.151 (1929).

LE-002 LE BLANC AND SACHSE, Z. ELECTROCHEM., VOL. 32, P. 204 (1926).

LU-001 LUNGE AND POLLITT, Z. ANGEW. CHEM., VOL. 15, P.1105 (1902).

LU-002 LUNGE AND REINHARDT, Z. ANGEW. CHEM., VOL. 17, P. 1041 (1904).

MA-004 W. MACHU, METALL UND ERZ, VOL. 39, P. 495 (1938).

ME-002 MEYER AND ROTGERS, Z. ANORG. ALLG. CHEM., VOL. 57, P. 104 (1908).

NE-001 W. NERNST, LEHRBUCH DER PHYS. CHEM., 15TH EDITION, P. 766.

NE-002 B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 696-734 (1928).

NE-003 B. NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE , VI.,' Z. ELECTROCHEM., VOL. 41, PP. 589-93 (1935).

BIBLIOGRAPHY (CONTINUED)

NE-004 B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).

NE-005 B. NEUMANN, E. GOEBEL, 'DIE ADSORPTION VON SCHWEFLIGER SAURE AN PLATIN, EISENOXYD UND CHROMOXYD, II.,' Z. ELECTROCHEM., VOL. 30, PP. 672-82 (1933).

NE-006 B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

PA-003 'DECOMPOSITION THERMIQUE DU SULFITE DE ZINC HYDRATE,' BULL. SOC. CHIM. FRANCE, VOL. 8, PP. 1749-56 (1964).

PE-002 V. PECHKOVSKII, A. KETOV, 'A STUDY OF THE THERMAL DECOMPOSITION OF ZINC SULFITE,' J. APPL. CHEM., VOL. 33, PP.1724-9 (1960).

RE-004 R. RAMIREZ, 'GYPSUM FINDS NEW ROLE IN EASING SULFUR SHORTAGE,' CHEM. ENG., NO. 4, P. 112, (1968).

SC-005 R. SCHENCK, H. ROTERS, 'UEER DIE AKTIVIERUNG VON OXYDEN DURCH FREMDOXYDE,' Z. ANORG. CHEM., VOL. 211, PP. 65-92 (1933).

SC-006 R. SCHENCK, Z. ANGEW. CHEM., VOL. 49, P.649 (1936).

SC-007 N.G. SCHMAHL, F I A T REVIEW INORG. CHEM., VOL. 27, P.13.

SC-008 R. SCHENCK, 'KATALYTISCHE WIRKSAMKEIT UND GLEICHGEWICHT,' Z. ANORG. CHEM., VOL. 260, PP.154-60(1949).

SI-002 SIMON AND FEHER, Z. ELEKTROCHEM., VOL. 38, P. 143 (1932).

SU-002 A. SUCHOV, B. BOROK, Z. MOROZOVA, 'THERMAL DECOMPOSITION OF CERTAIN SULFATES IN A CURRENT OF STEAM,' J. APPL. CHEM. USSR, VOL. 32, P. 1646, (1959).

BIBLIOGRAPHY (CONTINUED)

TR-011 M. TRAUTZ, S. PAKSCHWER, 'ZUR KENNTNIS DER SULFID-SULFAT REAKTION,' J. PRAKT. CHEM., PP. 147-81 (1929).

WO-004 WOHLER AND MAHLA, ANN. CHEM. PHARM., VOL. 81, P. 255 (1852).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

10 May 1968 TECHNICAL MEMORANDUM 004-009-Ch6 T. Parsons

AVAILABILITY OF METALS AND METAL OXIDES

The following survey was carried out to determine the availability of metals and metal oxides for use in the removal of sulfur dioxide from flue gases. The data collected were domestic and foreign production figures, domestic prices, imports, and consumption rates for the metals listed in Table I and their oxides. Information on metal sulfates, sulfites, and carbonates was also collected when available, since oxides can be produced from these compounds.

On consulting the Bureau of Business Research, the Bureau of Economic Geology, the 1967 Statistical Abstract of the United States, a key to statistical data and sources published by offices of the U. S. government and others, and the Kirk-Othmer Encyclopedia of Chemical Technology it was discoverd that most sources give as a main reference the U. S. Bureau of Mines Minerals Yearbook. The publications of the Department of the Interior, Bureau of Mines, were found to be the most complete and up-to-date sources for metal and metal oxide production rates and price estimates. The Bureau of Mines publications used in this study were the 1965 Minerals Yearbook, Volumes I and IV and the 1967 and 1968 Mineral Industry Surveys, monthly, quarterly, and annual. When information was unavailable from these sources the Kirk-Othmer Encyclopedia of Chemical Technology was employed.

After the data is presented in a concise, consistent manner, an attempt will be made to interpret the relative availability of metals and their oxides. The results of the literature search are shown in Table II.

Several discrepancies exist in the manner of reporting production figures for metals and their compounds. All units, long tons; metric tons; pounds (av.); troy ounces; ounces (av.);

and grams, were converted to short tons using the conversion factors in Table III so that comparisons would be facilitated. The unit"tons" was assumed to be short tons. Production figures were described in the literature as weight percent of ores, concentrates, material recoverable from ores, primary materials, secondary materials, mine production, smelter production, or simply "production for 1967". An effort was made to present the correct description of the production figure in Table II. Mine and smelter production figures were combined. Price estimates were rounded off to three significant figures or the nearest ten cents. If the amount in the World Production column did not represent every country, a note was made. Note that although 1965 production figures are not equal to those for 1968, they serve as a good estimate when the 1968 figures are unavailable since they are almost always of the same order of magnitude.

TABLE I

lithium
beryllium
boron
sodium
magnesium
aluminum
silicon
potassium
calcium
scandium
titanium
vanadium
chromium
manganese
iron
cobalt
nickel
copper
zinc
gallium
germanium
arsenic
rubidium
strontium
yttrium
zirconium
niobium
molydenum
ruthenium
rhodium
palladium
silver
cadmium
tin
antimony
cesium
barium
lanthanum
cerium
hafnium
tantalum
rhenium
tungsten
iridium
lead
bismuth
thorium
uranium

TABLE II

Element or Compound	World Production (short tons/year)		U. S. Production, Stocks Imports or Consumption (short tons/yr.)		Price Estimate (dollars/short ton)		Source
	Year	Amount	Year	Amount	Year	Amount	
Aluminum	1965	7,418,546.					3
	1965	7,415,000.					1
			1965	P 2,754,000.			1
					1965	490.	1
Bauxite Al_2O_3	1965	40,824,051.					3
			1965	P 1,852,300.			1
			1965	C 15,158,080.			1
					1965	Avg. 15.0	1
					1965	87% 24.2-25.7	1
					1965	88% 32.4	1
					1965	60% 12.5	1
Alumina					1965	106.	1
Aluminum Sulfite $Al_2(SO_3)_3$					1965	43.8	1
					1965	Fe-Free 76.	1
Antimony	1965	69,446.					3
			1965	P (ore) 13,234.			1
					1965	Domestic 880.	1
						Foreign 860-1,160.	1
			1965	C 16,919.			1
Antimony Trioxide					1965	950-1,200.	1
Arsenic			1965	I 180.			1
				P 0.	1965	London 1,000-1,113.	1
Arsenic Oxide	1965	Free world 68,343.					3, 1
"white arsenic" As_2O_3					1965	95% 64.	1
					1965	95% in barrels 96.	1
					1965	refined 82.	1
					1965	refined in barrels 114.	1
			1965	I 15,525.			
Barium Oxide BaO					1965	288.	1
Barium Dioxide Ba_2O_2					1965	600.	1
Barium Sulfide BaS			1965	P 124,279.			1
			1965	C 120,325.			1

Element or Compound	World Production (short tons/year)		U. S. Production, Stocks Imports or Consumption (short tons/yr.)			Price Estimate (dollars/short ton)			Source
	Year	Amount	Year	Amount		Year	Amount		
Barium Carbonate						1965		112.	1
$BaCO_3$									
"Witherite"			1965	P	85,609.				1
				C	28,345.				1
Barium Sulfate $BaSO_4$	1965	3,802,970.[1]							3
"Barite"	1965	3,790,000.	1965	P	846,000.				1
			1965	C	1,388,000.[2,4]				1
						1965	95%	18.5	1
						1965	96%	19.0-23.5	1
						1965	83%-93%	11.0-16.0	1
						1965	"blanc fixe"[2]	156.-175.	1
Beryllium			1965	S	153.				1
						1965	97%	124,000.	1
						1965	"200"-grade powder	108,000.	1
						1965	ingot	134,000.-142,000.	1
Beryl $3BeO \cdot Al_2O_3 \cdot 6SiO_2$	1965	5,512.[3]							3
11%BeO	1965	5,700.[3]							1
			1965	C	5,845.				1
			1965	S	28,143.				1
							See footnote 4		1
Bismuth	1965	4,409.[5]							3
	1965	4,700.[5]							1
			1965	C	1,466.				1
						1965	refined	6,860.	1
Boron Oxide			1965	C	425,000.				1
Boron			1965	I	0.377	1965		7,330.	1
Cadmium	1965	13,900.	1965	C	5,216.	1965	sticks & bars	5,160.	1
				P	4,836.				
Calcium						1964	97%	4,100.	1
						1964	less than 1 ton	2,500.	1
						1964	99.9%	5,200.	1
Cerium						1965	99.5%-99.9%	150,000.	1
Ceric Oxide			1962	P	900.				4 V4
						1965	99.9%	8,000.	1

Element or Compound	World Production (short tons/year)		U. S. Production, Stocks Imports or Consumption (short tons/yr.)		Price Estimate (dollars/short ton)		Source
	Year	Amount	Year	Amount	Year	Amount	
Cesium			1962	P .0795			4
					1962	small lots 99.9% 600,000.- 750,000.	4
					1962	99.9% ton lots 250,000.	4
					1962	99.5% 200,000.	4
					1965	99.6% 200,000.-550,000.[7]	1
					1965	99.98% 250,000.-650,000.[7]	
Cesium Carbonate					1965	64,000.- 60,000.[7]	1
Pollucite (6 to 32% Cs_2O)			1965	P see footnote 3			1
			1960	P (Cs_2O) 5.			4
			1965	I see footnote 6			1
Chromium			1965	P 4,748.[8]			1
				S 1,779,000.[8]			1
Chromite Cr_2O_3 Ore	1965	5,370,000.					1
	1965	5,401,000.					3
			1965	C 1,582,000.			1
			1965	S 1,094,000.			1
					1965	Foreign 44-48% 17.9-31.3	1
			1966	I 1,864,000.[9]	1967	48-5% Cr_2O_3	2
			1966	C 1,461,017.	1967	$(\frac{Cr}{Fe} = \frac{3}{1})$ 27.6-31.7	2
			1967	I 1,240,621.	1967	$(\frac{Cr}{Fe} = \frac{4}{1})$ 32.6-35.7	2
			1967	C 1,349,213.			2
Cobalt	1965	17,637.					3
	1965	17,100.	1965	S 795.			1
			1965	C 6,798.	1965	3,000. - 3,300.	1
			1967				2
Cobalt Sulfate			1967	I 23.			2
Cobalt dioxide			1965	P 229.			1
			1967	P 243.			2
			1967	I 522.			2
Copper	1965	10,540,000.					3
	1965	11,620,000.	1965	P 2,754,540.			1
			1965	P (ore) 173,286,000.	1965	London 1,170.	1
					1965	Foreign-delivered 730.	1
					1965	Domestic 708.	1
					1965	Electrolytic 680.	1
			1967	P 1,132,982.	1967	Electrolytic-Domes. 758.	2
			1967	C 1,192,092.	1968	Electrolytic-Domes. 759.	2
			1967	I 330,346.			2
Copper Sulfate			1967	P 40,356.			2
			1967	S 4,074.			2

Element or Compound	World Production (short tons/year)		U. S. Production, Stocks Imports or Consumption (short tons/yr.)		Price Estimate (dollars/short ton)		Source
	Year	Amount	Year	Amount	Year	Amount	
Gallium			1965	I 1.12	1965	99.99%[7] 1,270,000- 860,000	1
			1965	P see footnote 3		99.999%[7] 1,360,000.- 970,000	1
						99.9999%[7] 1,540,000.-1,088,000	1
Germanium	1964	55-83[10]			1964	"first reduction" 229,000	4 V10
					1964	"Intrinsic" 245,000	4 V10
			1965	P 45.0			1
			1965	I .039			1
					1965	"first reduction" 227,000	1
					1965	"Intrinsic" 245,000	1
					1965	single crystal 508,000	1
Germanium Dioxide			1965	I 1.576		"high purity" 137,000	1
					1964	137,000	4 V10
Hafnium					1965	"Sponge" 150,000	1
					1965	"Bar & Plate" 276,000	1
Iridium			1965	P 0.203	1965	3,040,000.-3,680,000	1
			1965	S 0.574			1
			1965	C 0.298			1
			1965	I 0.339			1
					1967	4,958,000.-5,542,000	2
Iron Ore			1966	P 100,964,640.			2
			1967	P 94,298,400.			2
			1967	I 50,400,000.			2
	1965	679,122,080.	1965	P 98,383,040.	1965	8.5	1
			1965	C 147,714,560.			1
	1965	674,078,900.					3
Pig Iron	1965	370,605,000.	1965	P 88,207,000.	1965	57.0	1
Iron Oxide Pigments			1965	P 57,000.		60.0-440.[11]	1
Lead	1965	5,880,000.	1965	P"recoverable from ores" 301,147.	1965	New York 320.	1
			1965	P"primary of ores" 305,007.	1965	London 287.	1 & 3
			1965	P"U.S. Prod." 315,000.	1967	Avg. 280.	2
Lithium					1965	18,000.-22,000.	1
					1967	(100-lb. lots) 15,000.	2
Lithium Carbonate					1965	900.	1
					1967	(ton lots) 850.	2
Lithium Sulfite					1965	2,300. -2,500.	1

Element or Compound	World Production (short tons/yr.)		U. S. Production Stocks Imports or Consumption (short tons/yr.)			Price Estimate (dollars/short ton)			Source
	Year	Amount	Year		Amount	Year	Amount		
Magnesium	1965	175,267.							3
	1965	174,000.	1965	P	81,361.	1965		705.	1
			1965	C	69,222.				1
			1967	P	96,500.				2
			1967	C	117,000.				2
Magnesium Carbonate						1965		280.-290.	1
Manganese Ore (35% Mn)	1965	19,413,883.							3
			1965	P	29,258.				1
			1965	C	2,866,079.				1
			1965	I	2,575,229.	1965	46-48% Mn	0.64-0.67	1
			1967	I	2,100,000.	1967	46-48% Mn	0.65-0.66	2
Manganese			1967	I	2,000.	1967		597.	2
						1965	(Electrolytic)	577.	1
Manganese dioxide	1967	24,000.[12]							2
Molybdenum	1965	57,320.[13]							3
			1965	P	38,655.	1965		3,125.	1
			1967	P	44,000.	1967	(concentrate)	3,240.	2
Molybdenum Oxide						1967	(bagged)	2,800.	2
Nickel	1965	470,686.							3
			1965	P	16,188.				1
			1967	P	13,250.[14]	1967	"S" grade Powder	1,960.	2
			1967	C	175,000.	1967	Electrolytic	1,880.	2
			1967	I	141,000.				2
Nickel Oxide						1967	"Sinter 75"	1,770.	2
						1967	"Sinter 90"	1,780.	2
Niobium						1967	99.6% powder	20,000.-60,000.	4 V13
						1967	Ingot	60,000.	4 V13
Niobium Ore (oxide) Columbite 73% $(Nb,Ta)_2O_5$						1967		8,000.-3,000.[28]	4 V13
						1967	per ton of Pentoxide contained	2,000.	4 V13
Pyrochlore 59% Nb_2O_5						1967	Brazilian	2,200.	4 V13
Platinum Group	1965	101.							3
Metals[15]			1967	I	7.00[26]				2
Potash[16]	1967	oversupply	1967	P	3,320,000.[16]	1967	Potassium salts	20.0	2

Element or Compound	World Production (short tons/year)		U. S. Production Stock Imports or Consumption (short tons/yr.)		Price Estimate (dollars/short ton)		Source
	Year	Amount	Year	Amount	Year	Amount	
Rhenium	1967	0.15-25.[17]	1967	C .55	1967	(1st lb.) 1,300,000.	2
						thereafter 1,160,000.	2
			1967	I .004	1967	Sintered bar 1,600,000.	2
			1967	Utah Production 2.00		see footnote 27.	2
Rubidium			1965	P See Footnotes 3 & 6	1965	99.5% 1,630,000.-1,200,000.[7]	1
			1965	I none	1965	99.8% 1,810,000. -250,000.[7]	1
Rubidium Carbonate					1965	280,000.-78,000.[7]	1
Ruthenium			1965	P 0.134			1
			1965	S 0.402			1
			1965	I 0.281	1965	1,760,000.-1,920,000.	1
Scandium					1965	see footnote 28.	1
Scandium Oxide					1965	Domestic3,500,000.-5,170,000.[7]	1
					1965	United Kingdom 8,890,000.	1
Silicon			1965	P 96-99% 78,075.			1
			1965	S 4,728.			1
			1965	C 70,601.			1
					1965	98% 365.-380.	1
Silver	1965	8,606.					3
			1965	P 1,361.			1
			1967	P 1,026.	1967	38,062.-51,770.	2
			1966	P 1,498.			2
Sodium			1965	P 149,946.	1965	bulk at works 340.	1
					1965	fused (18,000.-lb. lots) 390.	1
					1965	12-lb. bricks 420.	1
Sodium Carbonate "Soda Ash"			1965	P "soda ash" 6,400,000.			1
					1965	58% Na_2O bulk 32.0	1
					1965	58% Na_2O bags 38.0	1
					1965	Light soda ash bulk 31.0	1
					1965	Light soda ash bags 37.0	1
			1967	P (Na_2CO_3) 1,705,000.	1967	23.4	2
Sodium Sulfate "salt cake"			1965	P (crude) 1,003,000.			1
			1965	P (anhydrous) 389,000.	1965	100% Na_2SO_4 "salt cake" 28.0	1
			1967	P 631,000.	1967	17.4	2
					1965	Rayon Grade (bulk) 34.0	1
					1965	Rayon Grade (bags,carlots) 38.0	1
						Anhydrous (bags, carlots) 56.0	1
Strontium	1965	9,302,394.[19]					3
			1965	See footnote 18			1

Element or Compound	World Production (short tons/year) Year	World Production (short tons/year) Amount	U. S. Production Stocks Imports or Consumption (short tons/yr.) Year	U. S. Production Stocks Imports or Consumption (short tons/yr.) Amount	Price Estimate (dollars/short ton) Year	Price Estimate (dollars/short ton) Amount	Source
Strontium Sulfate			1965	I ($SrSO_4$ & $SrCO_3$) 9,741.	1965	90% 66.2 - 56.7	1
Celestite Ore (93%)			1965	S 93% 12,500.			1
Strontium Carbonate					1965	drums 700.-740.[7]	1
					1965	tech. grade 380.	1
Tantalum	1965	7,440.[20]	1965	P 356.[20]			1
	1965	7,716.[20]					3
					1965	Powder 60,000.- 98,000.	1
					1965	Sheets 94,000.-120,000.	1
					1965	Rods 104,000.-130,000.	1
Tantalite O e $(\frac{Ta_2O_5}{Nb_2O_5} = \frac{3}{1})$					1965	per ton of contained pentoxide 15,000.- 16,000.	1
Thorium					1965	Pellets 30,000.	1
Thorium Oxide					1965	99.9% Ceramic 11,600.-14,000.	1
					1965	high density 16,600.-20,000.	1
Monazite Ore (66-55% rare earth oxides)	1965	7,589.			1965	160.-240.	1
Tin	1965	440,384.					3
			1965	P 53.0	1965	2,395.	1
	1967	78,400.[21]	1967	P Texas 3,060.			2
			1966	C 95,744.	1968	3,060.	2
Titanium-Ilmenite $FeO \cdot TiO_2$	1965	2,728,217.[22]					3
			1965	P 948,832.			1
					1967	18.7-21.4	2
Titanium-Rutile TiO_2	1965	242,508.[22]					3
			1965	P 10,037.			1
					1967	119.-121.	2
Titanium			1967	I (sponge) 8,125.	1967	USSR (sponge) 2,000.	2
			1967	C (sponge) 20,062.	1967	Japan (sponge) 2,500.	2
			1967	P (ingot) 25,960.			2
			1967	C (ingot) 25,380.			2
Tungsten			1965	P concentrates (60% WO_3) 7,949.			1
	1965	Concentrates 60% WO_3 59,524.					3
			1965	P s.t. of contained W 6,233.			2
			1966	P s.t. of contained W 7,382.			2
			1967	C W concentrate 7,500.			2
			1967	I W concentrate 950.	1967	(metal) 35.-45.	2

Element or Compound	World Production (short tons/year)		U. S. Production Stocks Imports or Consumption (short tons/yr.)		Price Estimate (dollars/short ton)		Source
	Year	Amount	Year	Amount	Year	Amount	
Uranium (ore as U_3O_8)	1965	Free world U_3O_8 20,944.					3
			1965	P (ore) 4,362,614.			1
			1967	P (U_3O_8) 10,140.	1967	Avg. price on market (U_3O_8) 12,000.	2
			1967	I (U_3O_8) 764.[30]			2
Vanadium	1965	Free world 8,818.	1965	P 5,226.			1 & 3
			1967	P 6,000.			2
			1967	C alloys, metal, chemicals 5,000.			2
Vanadium pentoxide			1967	P (5,994. contained V) 10,700.	1967	(contained V_2O_5) 2,400.-2,600.	2
Zinc	1965	8,989,337.[23]					3
			1965	611,153.	1965	292.	1
			1967	P (recoverable) 546,420.			2
			1967	P (slab) 1,010,736.			2
			1967	I (ore) 534,000.			2
			1967	I (slab) 221,000.			2
			1967	C (slab) 1,220,000.	1967	240.-280.	2
Zinc oxide			1967	P Pb-free 187,170.	1967	leaded 35% 315.	2
			1967	P leaded 9,699.	1967	leaded 50% 330.	2
					1967	Pb-free 305.	2
					1967	French process 350.-355.	2
Zirconium			1965	P See footnote 3	1965	Sponge 10,500.-12,500.	1
			1965	I 58,873.	1965	Strip 22,000.-36,000.	1
			1965	C 35,500.	1965	Plate 20,000.-32,000.	1
			1965	S 42,900.	1965	Bars 22,000.-30,000.	1
Zirconium Oxide			1965	P 4,100.			1
			1965	S 1,090.			1
					1965	660.-3,000.[31]	1
Yttrium					1965	408,000.-1,000,000.	1

TABLE III

CONVERSION FACTORS

1 long ton = 1.12 short tons

1 metric ton = 1.10231 short tons

1 troy ounce = 3.42857×10^{-5} short tons

1 pound (av.) = $5. \times 10^{-4}$ short tons

1 ounce (av.) = 3.125×10^{-5} short tons

1 gram = 1.10231×10^{-6} short tons

Lange *Handbook of Chemistry*

The prefixed letters in the U. S. Production column (Table II) indicate the following:

C - Consumption figure
P - Production figure
I - Import figure
S - Amount of the commodity Stockpiled by producers, dealers, or U.S. Government.

FOOTNOTES

1. World production excluding Bulgaria.

2. Mineral $BaSO_4$ is Barite; artificial $BaSO_4$ is "blanc fixe".

3. 1965 U.S. production withheld or company confidential.

4. According to source I, "prices for domestic and imported beryl were on a buyer and seller basis."

5. Excluding U.S. and U.S.S.R. data, production figures unavailable or confidential.

6. 1965 U.S. import figures unavailable to Department of Interior, Bureau of Mines. Domestic producers are American Potash and Chemical Corporation, Trona, California; Dow Chemical Company, Midland, Michigan; and NSA Research Corporation, Callery, Pennsylvania.

7. Price depends on lot size.

8. Includes chromium briquets, chromium metal and miscellaneous alloys.

9. U.S. depends solely on imports from Southern Rhodesia, South Africa, Turkey, and Russia.

10. An estimate, not fully reported.

11. Price depends on color.

12. Japanese production only. Japanese consumption is 7,000 tons per year; the rest is exported.

13. Excluding Argentina, North Korea, Nigeria, Rumania, Southwest Africa, and Spain.

14. In units of Nickel contained in ferroalloys.

15. Combined data for Platinum, Palladium, Rhodium, Iridium.

16. K_2O equivalents.

17. Production of West Germany only.

18. King Laboratories, Inc., Syracuse, N.Y., is the only domestic producer. The company uses all the metal it produces.

19. Free world production of "strontium materials", excluding West Germany.

20. Includes Columbium production.

21. Production of Malaysia only.

22. Excluding U.S.S.R.

23. Excluding Czechoslovakia and Rumania.

24. Some $BaCO_3$ included.

25. Price varies according to quality of ore.

26. First three quarters of 1967.

27. Imported Rhenium sold at $40,000 per short ton less than domestic.

28. Sold in foil or sheets from .003 to .06 inches thick. Prices range from $18.00 to $10.50 per square inch based on a theoretical weight of .0499 grams per square inch of thickness.

29. There was no domestic mine production in 1965. Production figure denotes stockpile releases necessary because of shortages.

30. Through October, 1967.

31. Price depends on form and purity.

SOURCES	NUMBER IN TABLE II
Encyclopedia of Chemical Technology, Kirk-Othmer, Second Edition, Interscience Publishers, John Wiley & Sons, Inc., New York.	4
"International Review", *Minerals Yearbook*, Volume IV, U. S. Department of Interior, Bureau of Mines, 1965.	3
"Minerals and Metals", *Minerals Yearbook*, Volume I, U. S. Department of Interior, Bureau of Mines, 1965.	1
Mineral Industry Surveys, U. S. Department of Interior, Bureau of Mines, 1967, 1968.	2

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

April 11, 1969 G. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch22

MIXED METAL OXIDES

This memorandum describes a method for predicting the best mixed metal oxides to be used for sorbing sulfur oxides from flue gases.

Theoretically, it is possible to combine single metal oxides to form a group of metal oxides referred to as mixed metal oxides. The U. S. Bureau of Mines developed a sulfur removal process utilizing alkalized alumina, a mixed oxide consisting of sodium and alumina. It was found that by combining certain oxides the resulting oxide exhibited a greater thermodynamic potential for use as a sorbent than either of the single metal oxides alone.

Due to the numerous possibilities of combining single metal oxides to form mixed metal oxides a method of predicting the best combinations was developed.

It was first assumed that the difference in the free energy change for the mixed metal oxide and the single metal oxide was dependent upon the change in heat of reaction and that the change in entropy was essentially constant.

The decomposition reaction for single metal oxides is represented by:

$$MeSO_4 \rightarrow SO_3 + MeO \qquad (1)$$

An example of this reaction is given in Figure 1.

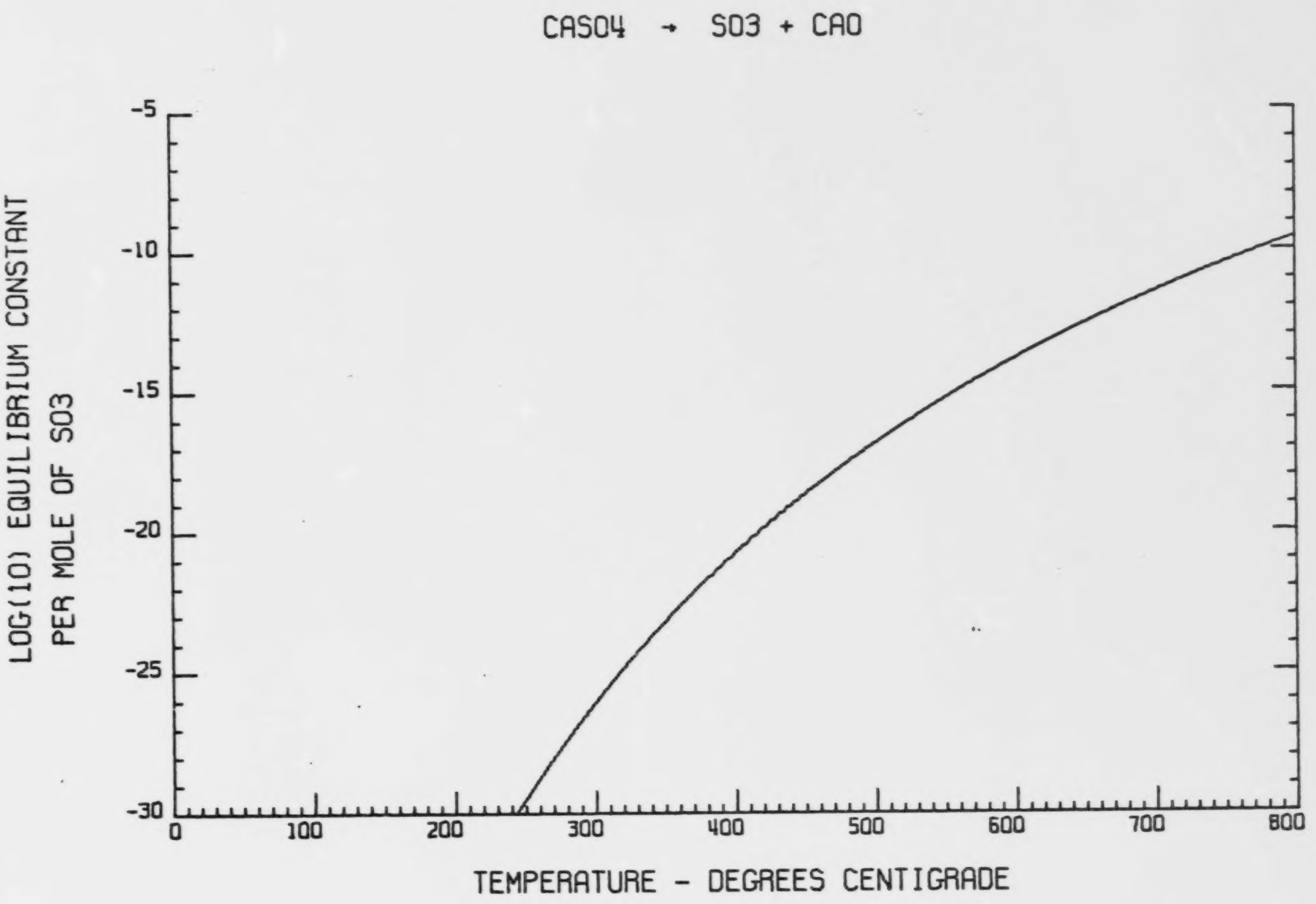


Figure 1

21 OCT 68

TRACOR

The Gibbs free energy change for the above reaction is given by:

$$\Delta G_1 = -2.3\ RT \log K_1 = \Delta H_1 - T\Delta S_1 \qquad (2)$$

The decomposition reaction for mixed metal oxides is represented by:

$$MeSO_4 + Me'O \rightarrow SO_3 + MeMe'O \qquad (3)$$

An example of this reaction is given in Figure 2.

The Gibbs free energy change for the above reaction is given by:

$$\Delta G_2 = -2.3\ RT \log K_2 = \Delta H_2 - T\Delta S_2 \qquad (4)$$

Subtracting equation (2) from equation (4) yields

$$\Delta G_2 - \Delta G_1 = -2.3\ RT \log K_2 + 2.3\ RT \log K_1 =$$

$$\Delta H_2 - T\Delta S_2 - \Delta H_1 + T\Delta S_1$$

which rearranges to

$$\Delta H_2 - \Delta H_1 = 2.3\ RT \left(\log K_1 - \log K_2 + \frac{\Delta S_2 - \Delta S_1}{2.3R}\right) \qquad (5)$$

It was found that $\frac{\Delta S_2 - \Delta S_1}{2.3R}$ was approximately equal to one, therefore, equation (5) can be written as

$$\Delta H_2^R - \Delta H_1^R = 2.3\ RT\ (\log K_1 - \log K_2 + 1) \qquad (6)$$

$\Delta H_2^R - \Delta H_1^R$ is also equal to ΔH_{ij}^R, the heat of reaction of the mixed metal oxide formed from the two separate single metal oxides.

ΔH_{ij}^R can be calculated by the following equation given by Erdõs (ER-001) and described in detail in T.M. 004-009-Ch1A.

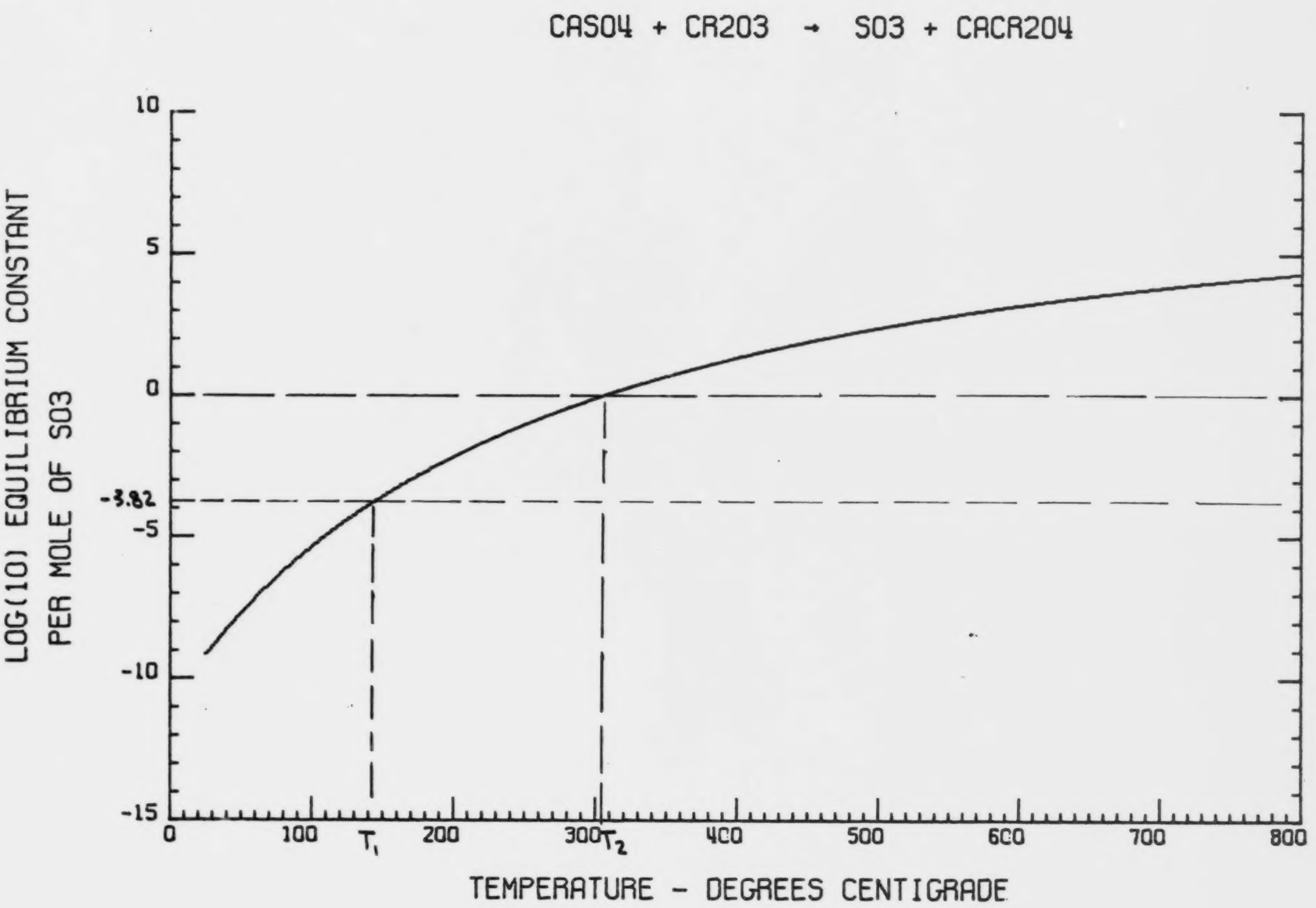


Figure 2

11 OCT 68

TRACOR

$$-\Delta H^{R}_{ij} = B_{ij}(K_i - A_j)^{N_j} \qquad (7)$$

The symbols are defined as follows:

i	ith cation species
j	jth anion species
B_{ij}	number of ion pair bonds formed
K_i	cation combining power
A_j	anion combining power
N_j	anion exponent
ΔH^{R}_{ij}	heat of reaction of oxide containing ith cation and acid containing ith anion

Rearranging equations (6) and (7) and solving for ΔlogK gives

$$\Delta \log K = \log K_1 - \log K_2 = \frac{\Delta H^{R}_{ij}}{2.303RT} \qquad (8)$$

Figure 1 represents a compound that thermodynamically has no chance of being used as a sorbent in a sulfur oxide removal process, whereas Figure 2 represents a compound that is thermodynamically feasible to be used as a sorbent. Since the ΔH^{R}_{ij} values are already known (T.M. 004-009-Ch1A) it is possible to predict the ΔlogK for all combinations of metal oxides. A comparison of predicted ΔlogK values from equation (8) and calculated ΔlogK values are given in Table II.

The thermodynamic screening process that was performed on the single metal oxides applies to the mixed metal oxides. The mixed metal oxides represent a more promising area for sorbent possibilities than the single metal oxides. However until a complete study and analysis is made on the mixed metal oxides no final conclusion can be drawn.

Table 1 gives a list of the most promising mixed metal oxides in decreasing order to be used for sorption of sulfur oxides from flue gases and also having the best regenerative possibilities.

Gary P. Schroeder

TABLE I

MOST PROMISING MIXED METAL OXIDES

Compound	Log K at 750° C
$Mn(Cr_2O_4)_3$	6.34
$Sn(MoO_4)_2$	6.24
$Bi_2(V_2O_6)_3$	6.16
$Al_2(Cr_2O_4)_3$	4.52
$U(V_2O_6)_2$	4.36
$Fe_2(Cr_2O_4)_3$	4.25
$CaCr_2O_4$	4.02
$Sb_2(Cr_2O_4)_3$	3.94
$CoMoO_4$	3.59
$Sb_2(V_2O_6)_3$	3.25
$Fe_2(V_2O_6)_3$	2.91
$BeMoO_4$	2.67
$Li_2Cr_2O_4$	2.57
$Al_2(V_2O_6)_3$	2.55
$NiMoO_4$	2.28

TABLE II

ΔLOG K MIXED METAL OXIDE PREDICTIONS

Oxide	$\log_{10}K$ Sulfate Decomp. 750° C	$\log_{10}K$ Mixed Oxide Decomp. 750° C	ΔlogK 750° C Actual	ΔlogK 750° C Predicted
CaO	-10.45	+ 4.31 $CaCr_2O_4$	14.76	14.53
CuO	- 1.14	- 0.004 CuV_2O_6	1.136	0.77
CuO	- 1.14	- 0.54 $CuAl_2O_4$	0.6	0.146
Fe_2O_3	+ 0.39	+ 2.13 $Fe_2(V_2O_6)_3$	1.74	2.52
Na_2O	-20.3	-11.1 $Na_2Al_2O_4$	9.2	9.09
Na_2O	-20.3	- 2.62 $Na_2V_2O_6$	17.7	16.15
NiO	- 2.77	+ 0.618 NiV_2O_6	3.39	2.6
ZnO	- 2.94	+ 2.54 $ZnMoO_4$	5.48	4.4

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

29 May 1969

TECHNICAL MEMORANDUM 004-009-Ch25

"STATUS OF MIXED METAL OXIDE STUDIES"

The goals of TRACOR contract PH 86-68-68 were to determine the feasibility of using single or mixed metal oxides to remove sulfur oxides from furnace flue gases. This memorandum gives the status of the mixed metal oxide work. The task of finding the best oxides of the 48 metals considered was divided into two parts.

The first part consisted of surveying the existing knowledge, compiling the thermodynamic properties of compounds of interest, and using these properties to determine the most thermodynamically favorable sorbents. The result of the thermodynamic screening was a list of potential single metal oxide sorbents. An estimation method outlined in TM 004-009-Ch22 indicated that some mixed metal oxides might have good sorption capabilities as well as more favorable thermal regeneration capabilities.

The second part was carried out to determine the rate of reaction of the potential metal oxide sorbents with SO_2 under flue gas conditions. This task involved.the characterization of each metal oxide by x-ray diffraction, BET surface area determinations, and chemical analysis. Such characterization is essential since the kinetic activity of a sample is highly dependent on its method of preparation and the resulting physical properties.

The results obtained to date in the single metal oxide sorption study show that the approach outlined above is a successful way to determine the best potential single metal oxide sorbents.

Assuming the correct reactions are written for the compounds of interest, thermodynamic screening should also be a successful way to determine the potential mixed metal oxide sorbents. Very little is known, however, about the reactions which might occur in the mixed metal oxide - SO_2 system. Preparing, characterizing, and structurally identifying mixed metal oxides and their reaction products would be a task of great magnitude as opposed to the relative ease of preparation, analysis, and characterization of single metal oxides. These facts are discussed in more detail in the Theoretical Discussion section below. Due to the anticipated complexity of experimental work with mixed metal oxides, work in this contract was focused on single metal oxides.

Theoretical Discussion

The reaction of metal oxides with sulfur oxides is a typical Lewis acid-base reaction, with oxide ions the base. The reversibility and thermal regenerability of the sorption reaction thus depend primarily on the electron pair properties of the oxide ions, which are in turn determined by the electrostatic character of the neighborhood of these ions in the lattice. Variations in this electrostatic character from metal ion to metal ion in the single metal oxides are extensive, and result in equilibrium constants which range over 40 orders of magnitude for the reaction with SO_2 and SO_3. The equilibrium constants are, nevertheless, rather distinctive for a given single metal oxide, even though some variation in the stoichiometry of most of these oxides is the normal, rather than the exceptional case (e.g., FeO is always stoichiometrically deficient in Fe). Despite the variability, we can be reasonably confident that the equilibrium constants as obtained from the thermodynamic calculations will apply. We do not believe this to be the case with the mixed metal oxides. From a theoretical study just completed, we conclude the following:

1. Calculations according to the Erdös method as per TM 004-009-Ch22 may give a "ball-park" estimate of the equilibrium constants for reaction (1).

$$MeO + Me'SO_4 \rightleftharpoons MeMe'O + SO_3 \qquad (1)$$

It is probably too much to expect, however, that a simple mixture of one metal as the sulfate and the other metal as the oxide would be formed in the sorption step (i.e., the reverse of reaction 1). Taking as an example of simple cubic spinel $CuFe_2O_4$, the sorption reaction with SO_3 can be written:

$$CuFe_2O_4 + SO_3 \rightarrow CuSO_4 + Fe_2O_3 \qquad (2)$$

$$CuFe_2O_4 + 2SO_3 \rightarrow CuO + Fe_2(SO_4)_3 \qquad (3)$$

$$CuFe_2O_4 + 3SO_3 \rightarrow CuSO_4 + Fe_2(SO_4)_3 \qquad (4)$$

In order to be able to use this mixed oxide according to Equation (3), the CuO formed must be inert toward SO_3 at the sorber temperature, $Fe_2(SO_4)_3$ must decompose at the regeneration temperature, and the oxide product of the decomposition must recombine with the CuO to regenerate the original spinel. If all of these conditions are not met, the mixed oxide can be no better than a physical mixture of the two separate oxides.

2. Both the structures and the stoichiometries of the mixed oxides, and thus the Lewis base character of the oxide ion, can

vary over wide ranges for a given pair of metal ions. Thus, well defined stoichiometries like $BaFe_{15}O_{23}$, having a definite structure, and $BaFe_{18}O_{27}$, having a definite but different structure, are not uncommon in the spinels. Before investigating any of the mixed oxides experimentally, it would be well to recognize that a great deal of crystalline structural determinations would have to be made at all stages of the sorption-regeneration cycle, since the reaction mechanisms have not been established.

3. Considering the wide range of metal ion pairs available plus the varieties of stoichiometries and structures available, it is almost inconceivable that one cannot find some (maybe several) mixed oxides with exactly the desired sorption and regeneration temperatures and equilibrium constants. Thermodynamic and theoretical screening can be an aid in selecting them, but it will simply take a lot of work to prepare, to characterize, and to find one or two with stability through cycling. To study this subject properly will be an undertaking of a considerable magnitude. While some mixed metal oxides show theoretical promise, we have already demonstrated both theoretically and experimentally an equally great promise for certain single metal oxides. These are almost certain to be simpler in operation and also easier to prepare and handle than the mixed oxides. Perhaps it should be emphasized at this point that the foregoing is not a recommendation to drop consideration of the mixed oxides from the overall HEW program. Rather it should be recognized that the entire concept is somewhat complicated from a theoretical standpoint, and it will require a thorough and comprehensive study plus some careful experimental work to do it justice.

In view of the promising experimental outlook for some of the single metal oxides and the probable simplicity of their reactions with SO_x, it is recommended that work in the immediate future be concentrated in this area. The mixed oxide concept should be kept in reserve for future development if unforeseen difficulties arise in using single metal oxides.

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

8 April 1969 Terry B. Parsons

TECHNICAL MEMORANDUM 004-009-Ch23

COMPUTER PROGRAMS FOR THE STUDY OF SULFUR OXIDE REMOVAL BASED ON DRY METAL OXIDES

I. INTRODUCTION

This paper gives a brief qualitative description of each of the computer programs used for data retrieval, thermodynamic property estimation, processing of experimentally obtained data, and determination of cost and design of the fluidized bed system.

II. PROGRAMS FOR DATA RETRIEVAL

The thermodynamic properties for metals and their compounds are stored and retrieved for use in calculations by the program AIRPOL. Each compound is characterized by a "data set" that contains the following properties:

1) Heat of formation at 25° C
2) Standard entropy
3) Coefficients for the heat capacity equation
4) Heats and temperatures of phase transitions
5) Sources from which each of these data were obtained.

Each data set is input by the user, and it may be in units of calories, kilocalories, joules, or kilojoules. Any part of the data set for each compound may be changed or deleted from the data base, or the data base may be printed (output) in several forms by the user for checking or reporting. A table of contents listing names of compounds for which there are data stored may be printed either on request or each time maintenance is carried out. References are printed with each data set in the form of six-character code names input by the user. A bibliography giving the code names and the source to which they refer is printed on request. The program AIRPOL uses the stored data to calculate entropy and enthalpy changes and the logarithm of the equilibrium constant at any temperature for any reaction involving compounds for which a data set has been input. The enthalpy and entropy changes for the reactions and the logarithm of the equilibrium constant can also be plotted as a function of temperature for any temperature range for which data are stored.

Using the program PRNTAL, the user can obtain a copy of the thermodynamic properties of all 629 compounds and the references printed in easily read, tabular form. The heats of formation, standard entropies and phase transition data are printed in one table along with the reference code names. The heat capacity coefficients are printed in a separate table with the reference code names. A table of contents and a bibliography listing are also printed by PRNTAL.

Program BIBHAL maintains a data file of coded, six-character reference names which refer to bibliography entries input by the user. The code name is formed by using the first two letters of the author's last name and three numbers. After the data are input, a bibliography listing in a form suitable for a final report can be obtained by inputting the code names for the references to be printed. The entire bibliography can also be printed at one time. The bibliography data file may be kept up-to-date by adding, deleting or replacing references. There are presently 209 references on the bibliography data file, and there is a maximum capacity of 700 references.

III. PROGRAMS FOR THERMODYNAMIC PROPERTY ESTIMATION

Program HTCAPY estimates the heat capacities of mixed metal oxides by adding the heat capacity coefficients of the constituent single metal oxides. The single metal oxide heat capacity data stored previously by AIRPOL are retrieved by HTCAPY when the user inputs the compound names of the constituent oxides. The resulting estimated mixed oxide heat capacity coefficients are printed in tabular form along with the temperature ranges of validity.

The program HTCAPS estimates the heat capacities of metal salts such as sulfates, carbonates, and sulfides from the known heat capacities of metal oxides according to the theory and derivation in T.M. 004-009-Ch13. The oxide heat capacity coefficients are subtracted from known heat capacity coefficients for the corresponding metal salt and a heat capacity increment for the remaining anion is calculated by a least squares method. When the increment ΔCp for a particular anion is added to an oxide heat capacity the result is the estimated heat capacity for a metal salt. For instance, by subtracting known oxide heat capacities from the known corresponding metal sulfate heat capacities an increment for the heat capacity of the SO_3 oxyanion is obtained. The increment can then be added to metal oxide heat capacities for which the corresponding metal sulfate heat capacity is unknown to estimate the heat capacity. Program HTCAPS retrieves heat capacity data previously stored by AIRPOL for metal oxides and metal salts, calculates the increment ΔCp for each anion, estimates the unknown heat capacities, and calculates an error by comparing known and estimated values. The heat capacity coefficients are printed in tabular form with the temperature range of validity.

Program HECACF correlates tabularized heat capacity-temperature data with the equation form $Cp = A + B \cdot T + C \cdot T^2 - D/T^2$ using a least squares method. The heat capacity in calories or joules and the corresponding temperatures in degrees Kelvin or centigrade are input by the user and the coefficients A, B and either C (for a gas or liquid) or D (for a solid) are calculated. An error is calculated by comparing actual values at each input temperature to values computed with the coefficients.

The program ENTROP calculates known absolute entropies using several estimation methods and compares estimated and known entropy values. The entropy estimation methods all involve adding a cation and an anion entropy contribution. The anion entropy contribution for each anion of interest is determined using each estimation method and the error in this determination is calculated. Using ENTROP, the anion entropy contributions for all anions of interest were calculated. The method of Latimer was found to yield anion entropy values which cause the smallest error in estimated entropies. The program ENTROP retrieves known values of entropy previously stored by AIRPOL. Metal entropies are subtracted from known corresponding metal salt entropies and a correction is applied to determine average anion entropies.

The program FORM predicts the heat of formation of a compound from the known heats of formation of its constituent reactants and an estimated heat of reaction. The estimation method, proposed by ERDŐS (ER-002), is outlined theoretically and mathematically in T.M. 004-009-Ch1 and Ch1A. The known heats of formation, stored previously by AIRPOL, are retrieved from the Tracor data base. They are used in the Erdős method by FORM to estimate the unknown heats of reaction. Estimated heats are printed in tabular form along with the errors in estimated as compared to known values.

IV. PROGRAMS FOR PROCESSING EXPERIMENTALLY OBTAINED DATA

Tracor's experimental program involves collecting kinetic data for the SO_2 sorption reaction of selected metal oxides using thermal gravimetric analyses (TGA). The TGA data are in the form of weight of sorbed SO_2 vs. time. The program PLOTDB plots the kinetics data in eight different integral forms of the rate equation (extent of reaction vs. time). Visual inspection then indicates which form best fits the data. Then the user selects the best form and PLOTDB plots the data and fits a least squared regression line through it.

Another type of data collected at Tracor is surface area measurements on the oxides for which kinetic data are determined. The BET method is used. This method is well known and a derivation of the BET equation can be found in many physical chemistry textbooks. Program SSAREA calculates, using the BET equation, the specific surface area of a sample in square meters per gram from measurements of volume of adsorbate adsorbed at a measured pressure. The program uses a least squares method to fit the data to the linear form of the BET equation. The accuracy of the least squares fit is described in appropriate error calculations. Errors between calculated and actual values of STP volume adsorbed are also given. The input data and the results are printed in tabular form suitable for use in a formal report.

V. PROGRAMS FOR DETERMINATION OF COST AND DESIGN OF THE FLUIDIZED BED SYSTEM

Tracor has built a group of subroutines which computes the cost and design of a fluidized bed system. Each of the subroutines can be used independently, and the routines are also linked together by the driver program FLUID. Program FLUID inputs the necessary quantities required to operate each subroutine, and it prints the output returned by each subroutine called.

Subroutine FANCST computes the fan and driver motor costs required for the system from the pressure drop across the fan, the current cost index, and the air density at the operating temperature.

Subroutine SORBER computes the cost of the sorber system. This system includes the sorber shell, sorber heads, gas distributor, and sorber lining. The costs are computed from the current cost index, the inside sorber diameter, and the height and thickness of the shell.

Subroutine CYCLON determines the design and cost of the cyclone used to collect fines in the sorption units. The design and cost are determined from the flow rate, fluid and solid densities, the current cost index, the pressure drop, viscosity, and the cyclone removal efficiency.

Subroutine CAPTAL computes the capital investment costs for the system from the purchased equipment cost and the power input required. Subroutine OPER computes the operating costs for the system from information about the number and type of employees; various operating expenses; the cost of waste disposal; the amount of air, water, steam, and coal used; and the number of years of operation.

Subroutine FLUBED computes the dimensions of the vessel that houses the fluidized bed and calculates some of the properties that describe the operation of the fluidized bed. The basic information required is particle size and density, temperature pressure and velocity, bubble characteristics, flow rate, and reaction rate data.

BLANK PAGE

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

8.1 UNABRIDGED TECHNICAL MEMORANDUMS

8.1.2 Technical Memorandums on Kinetic Studies

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

25 October 1968 D. W. DeBerry

TECHNICAL MEMORANDUM 004-009-Ch10

TEMPERATURE CALIBRATION OF THE TRACOR DTA

I. INTRODUCTION

The R. L. Stone differential thermal analysis (DTA) apparatus to be used in determining thermodynamic data for metal oxide - CO_2, SO_2, or SO_3 reactions was temperature calibrated to obtain accurate data. This calibration was done by recording the thermograms of high purity metals with well defined melting points. The procedures used and parameters involved are discussed below.

II. APPARATUS

The basic apparatus consists of an R. L. Stone LB202 Recorder-Controller and JP202 Furnace Platform. The sample holders were a ring differential thermocouple type. The samples were placed on small foil pans that sit in the sample holder rings. Sample holders constructed of nickel and 446 stainless steel were calibrated. Both sample holders had platinel differential and reference thermocouple. Platinum pans 0.0015 inch thick and weighing ~ 25mg were used for the final calibration. The thermograms were recorded on a Moseley X-Y recorder, and transition temperatures were measured using scales supplied by R. L. Stone Co.

III. MATERIALS AND PROCEDURE

Preliminary investigation indicated that metals gave sharper and better defined melting points than most chemical compounds. Metals are also more readily available in high purity form. Tin, lead, aluminum, and silver all at 99.999% purity and obtained from A. D. Mackay, Inc., were used as standards.

The samples used for DTA were sliced so as to give good thermal contact with the sample pan. The amount of sample used was 1-2.5mg. Alumina was used as reference material. Prior to a calibration run, the reference temperature was electronically set at 0° C and a vertical mark was made on the paper with the X-Y recorder manual adjust. The thermogram for the material was then recorded at 5 and 20° C/min heating rates in a N_2 or Ar dynamic (50cc/min) atmosphere. A typical thermogram is shown in Figure 1.

IV. RESULTS

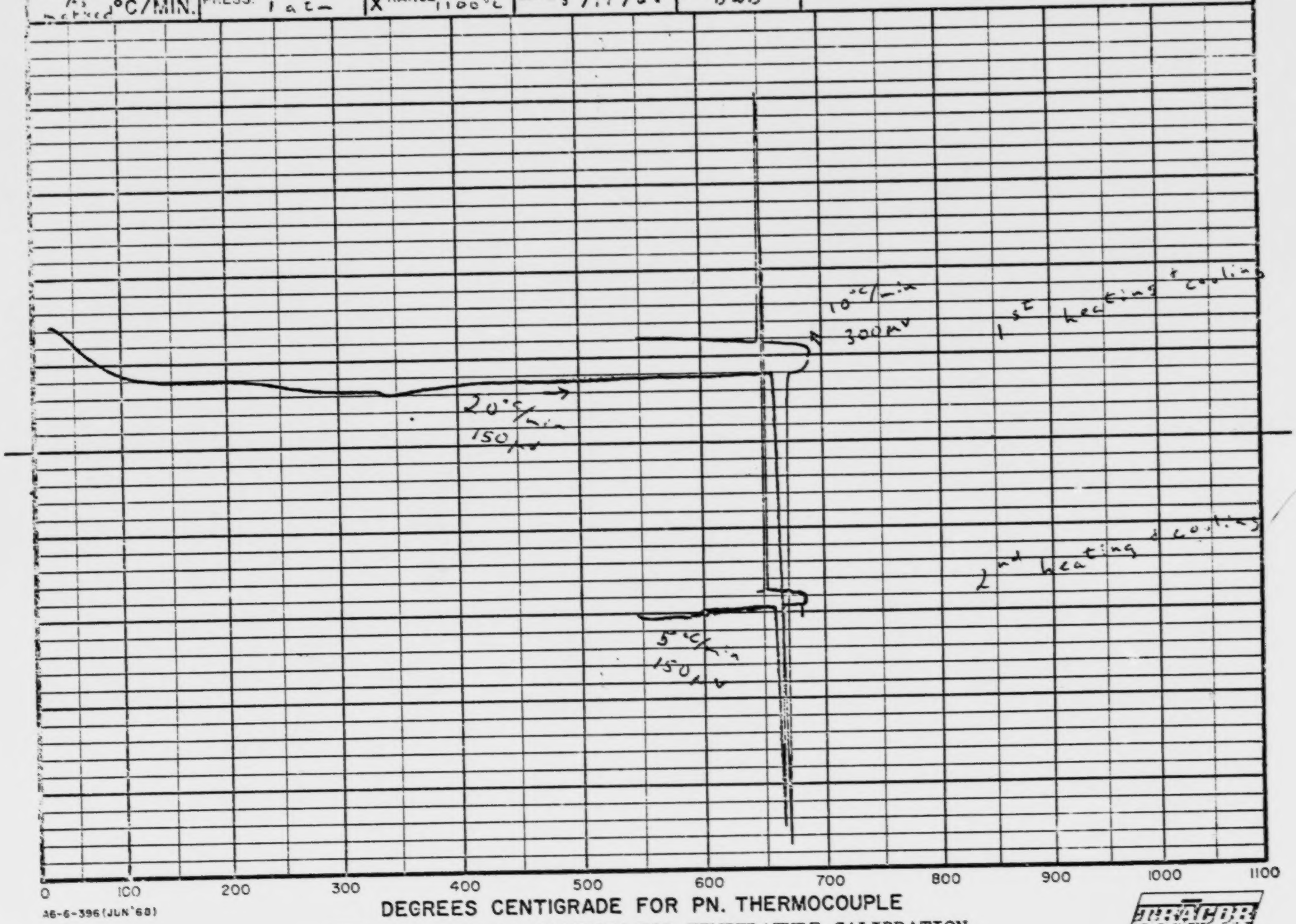
Since the metals used showed apparent supercooling effects, the melting points were used rather than the freezing points. All of the measurements indicate that the reference or recorded temperature value is lower than the actual sample temperatures. The error increases with temperature. It is over twice as large for the 446 stainless steel holder as for the nickel holder. The heating rate had little discernable affect on the recorded melting point.

Spot checks of the affect of other parameters on the error were done using AgCl which has a sharp melting point at an intermediate range temperature of 455° C. The measured melting point

1.07 mg alumina 6761

tube bel
ff 7.7 cm

MATL. Aluminum 99.999%	WT. 1.17 mg	SH-118 R-N2	Y RANGE as marked	GAS 1. N_2 2.	GAS FLOW 50 cc/min
As marked °C/MIN.	PRESS. 1 atm	X RANGE 1100°C	DATE 8/17/68	OPR: DWD	REMARKS:



A6-6-396 (JUN'68)

FIG. 1 - DTA OF ALUMINUM FOR TEMPERATURE CALIBRATION

was increased by $\sim$ 1°C by employing helium which has about ten times the thermal conductivity of Ar or N_2 as the dynamic gas. The measured melting point was increased $<$ 1°C by using an aluminum sample pan having the same shape as the platinum pan. The measured and accepted melting temperatures are given in Table I.

David Deberry

TABLE I

LITERATURE AND MEASURED MELTING POINTS OF HIGH PURITY METALS

		MELTING POINT, °C			
		MEASURED AT			
SAMPLE HOLDER	MATERIAL*	5°C/min	20°C/min	LITERATURE	ERROR
Nickel	Tin	230	230	231.85	1.8
(SH11BR2Ni, #6761)	Lead	325	325	327.4	2.4
	Aluminum	657-8	657-8	659.7	2.2
	Silver	957-8	957-8	960.5	3.0
466 Stainless Steel	Tin	227	227	231.85	4.8
(SH11BR2SS, #68100)	Lead	322	321	327.4	5.9
	Aluminum	654-5	654	659.7	5.2
	Silver	952	952	960.5	8.5

* All 99.999% Purity

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

21 February 1969

J. P. Nolley
P. S. Lowell

TECHNICAL MEMORANDUM 004-009-Ch20

GAS MIXING AND CONTROL EQUIPMENT

Experiments often require many different gas mixtures or gas mixtures which are not commercially available. A gas mixer was necessary for the study involving the removal of SO_2 from flue gasses. Although the apparatus which TRACOR has built was designed to simulate the composition of flue gasses as well as produce SO_3 for experimental purposes, it should be readily adaptable to other purposes.

A schematic diagram of the apparatus built at TRACOR is shown in Figure 1. The equipment may be divided into five sections: 1) a Gas Mixing Section where nitrogen, oxygen, carbon dioxide, and sulfur dioxide are mixed in the desired proportions and humidified; 2) a Reactor Section to convert SO_2 into SO_3 if necessary for certain experiments; 3) a Pressure Control Section to insure a constant manifold pressure; 4) an Experimental Equipment Section where mixed gasses are metered before entering the experimental apparatus and where pressure within the experimental apparatus is controlled; and 5) a Scrubbing Section to remove SO_2 and SO_3 from the exit streams before release to the atmosphere.

The front panel is shown in Figure 2. The components of the Gas Mixing Section are located on the right half of the panel. The pressure regulator (used in Pressure Control Section) is above the pressure gauge. The relief valves and two sample ports are

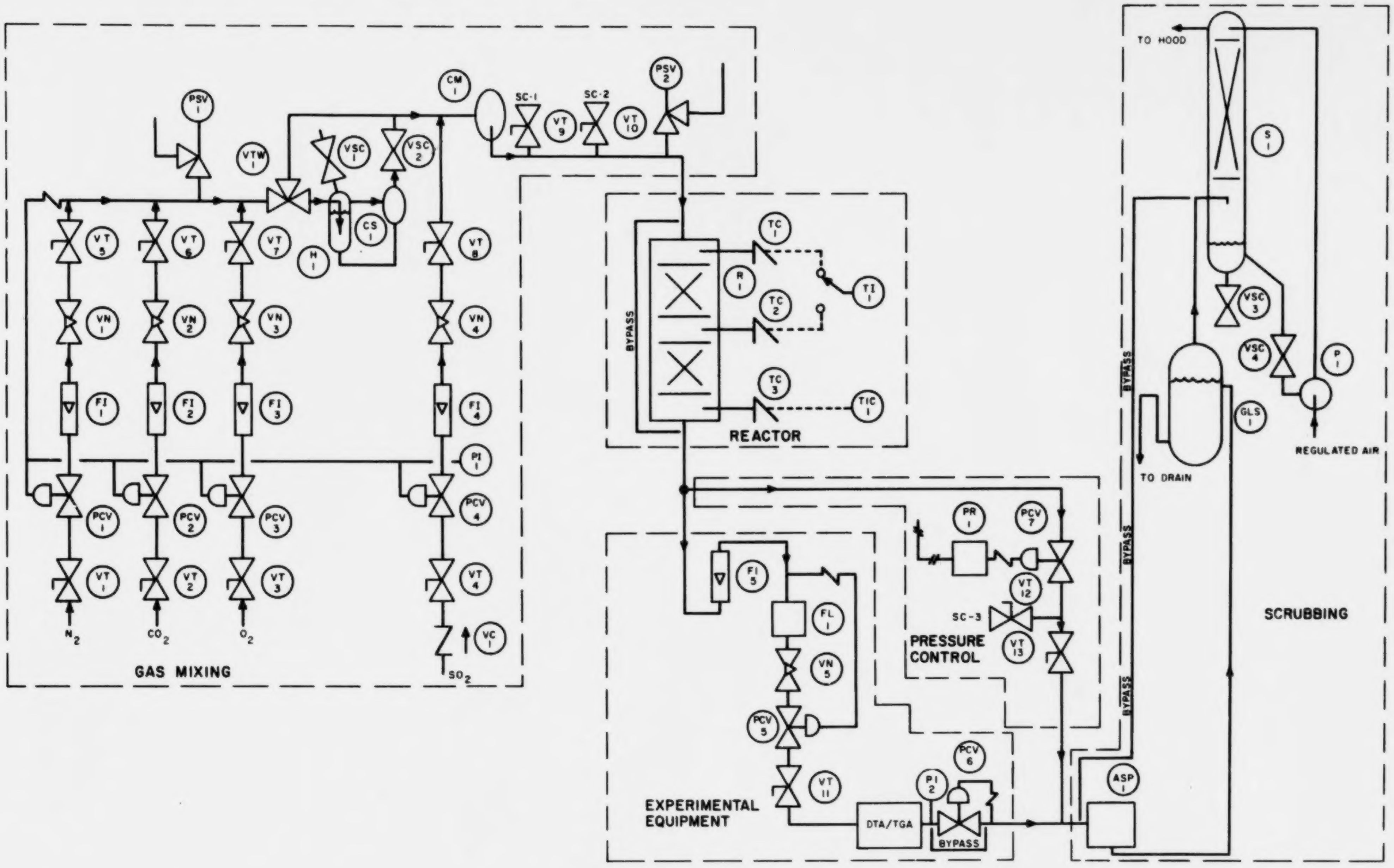

GAS MIXING
N2
CO2
O2
SO2
VT 1
VT 2
VT 3
VT 4
PCV 1
PCV 2
PCV 3
PCV 4
PI 1
VC 1
FI 1
FI 2
FI 3
FI 4
VN 1
VN 2
VN 3
VN 4
VT 5
VT 6
VT 7
VT 8
PSV 1
VTW 1
VSC 1
VSC 2
H 1
CS 1
CM 1
SC-1
VT 9
SC-2
VT 10
PSV 2
BYPASS
R 1
TC 1
TC 2
TC 3
TI 1
TIC 1
REACTOR
FI 5
FL 1
VN 5
PCV 5
VT 11
DTA/TGA
PI 2
PCV 6
BYPASS
EXPERIMENTAL EQUIPMENT
PR 1
PCV 7
VT 12
SC-3
VT 13
PRESSURE CONTROL
ASP 1
BYPASS
BYPASS
BYPASS
TO HOOD
S 1
VSC 3
VSC 4
P 1
GLS 1
TO DRAIN
REGULATED AIR
SCRUBBING

FIG 1 - SCHEMATIC DIAGRAM OF APPARATUS

TRACOR DWG B6-164-5
2/17/69 JM/LOWELL

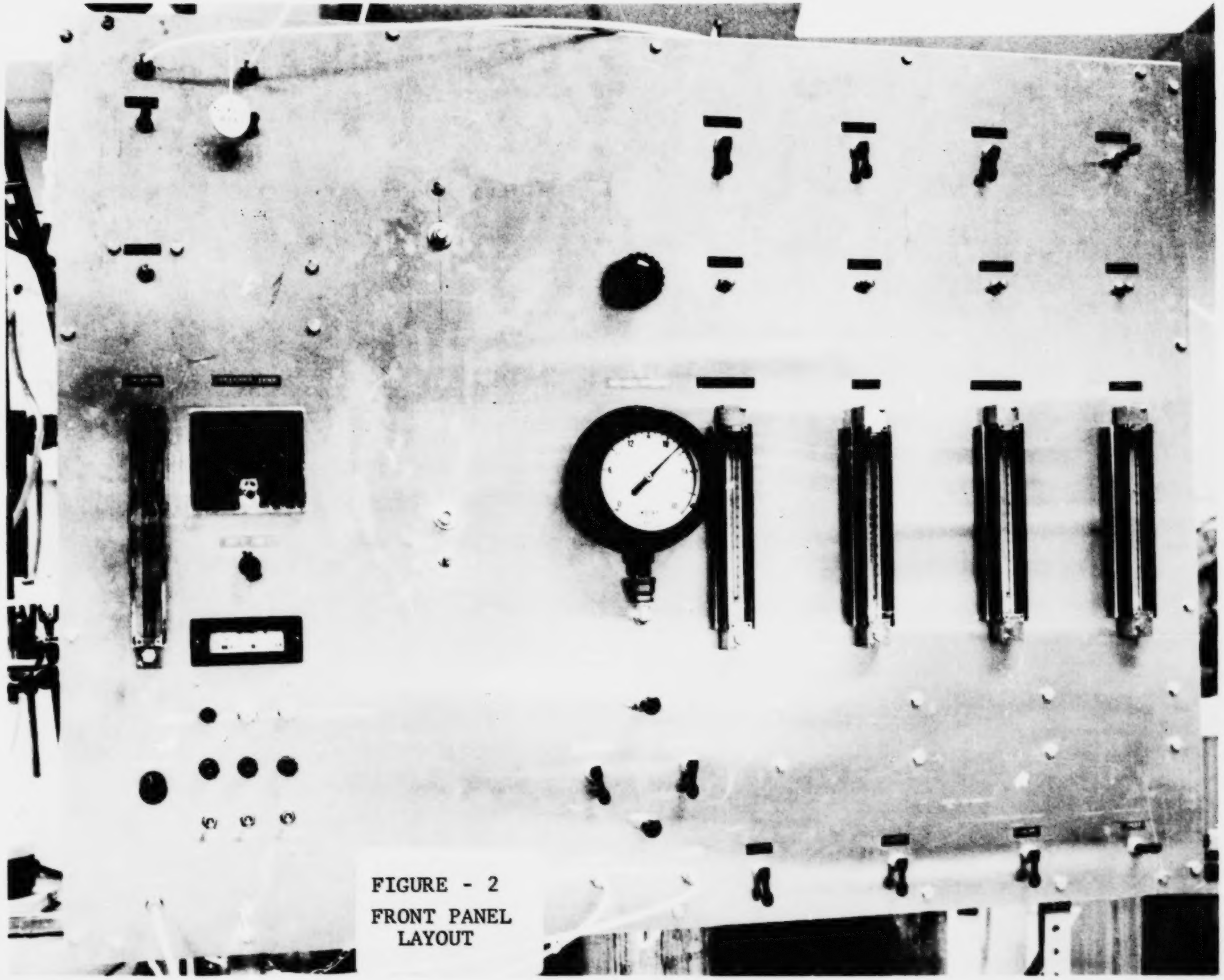


FIGURE - 2
FRONT PANEL
LAYOUT

below the pressure gauge. The electronic components to the left of the pressure gauge are used to monitor and control the reactor temperatures. The valve in the lower left controls the flow for the third sample port. The single rotameter on the left monitors the flow to the Experimental Equipment Section. The valve labeled outlet (top lefthand corner) is VT-11 which is in the line to the experimental equipment. The valve to its right is VT-13 which is in the excess gas line to the scrubber. Components downstream from these two valves are not mounted on the panel.

1) Gas Mixing Section

The Gas Mixing Section was used to mix and humidify four different gasses. The system was designed for nitrogen, oxygen, carbon dioxide, and sulfur dioxide. Since flue gas is simulated the flows in each stream are different. The only problem caused by this is that components in each stream must be sized differently. The nitrogen is introduced farthest upstream so that the system can be easily purged. Corrosion is a problem only after SO_2 and H_2O are mixed. The N_2, O_2, and CO_2 were humidified before introduction of SO_2. Consequently, the components of the Gas Mixing Section are made of brass. High density polyethylene tubing was used except where, for ease of construction, stainless steel tubing was used. The flow scheme illustrated in Figure 1 will now be described.

Nitrogen is delivered at 35 psig. The gas is passed through a toggle valve (VT-1). A toggle valve was used since it may be quickly turned on and off without changing the needle valve setting.

The 35 psig gas then passes through the control valve (PCV-1). The valve was chosen so that its usable flow range was greater than the flow range expected. The valve uses the manifold pressure as a reference. It maintains a 3 psi drop between its outlet and the manifold. The gas was then passed through a rotameter (FI-1) which was sized according to the expected flow range. The rotameters have two floats so that their usable range is better than 20:1. The needle valve (VN-1) has essentially a 3 psi drop across it. Characteristic curves for several valves at a 3 psi drop were compared. A valve with a large number of turns and good control for the desired flow range was selected. In addition, the constant pressure drop allows flows in each stream to be set without affecting the flows in the other streams. Once a flow is set, the flow will return to its original value after turning the gas off and on with the toggle valves. A toggle valve (VT-5) was installed before the manifold to provide quick on-off control when desired. A pressure relief valve (PSV-1) was installed to protect the components upstream from the three way valve at the humidifier.

A humidifier (H-1) was built in our glassblowing shop. It consists of a gas dispersion tube mounted axially inside of a larger tube. The larger tube holds enough water for one day's operation. A cyclone separator (CS-1) was installed to remove entrained water. A line between the cyclone and humidifier serves as a water return line. Two valves (VTW-1, VSC-2) allow the humidifier to be bypassed.

A cyclone mixer (CM-1) was installed to insure complete mixing of the gases in the manifold. Two sample ports (SC-1, SC-2) were installed at the downstream end of the Gas Mixing Section. One is used for an Orsat analysis; the other is used for Reich's test for SO_2. A pressure relief valve (PSV-2) was installed to protect components downstream from the three way valve. Its release pressure was set below the test pressure of the glass components.

Figure 3 is a rear view of the Gas Mixing Section. The nitrogen bottle is in the foreground. The nitrogen flows upward along the panel. The humidifier is shown between the oxygen and SO_2 streams. The bend in the tubing that extends beyond the top of the panel serves as a trap to prevent water condensate from dripping into the SO_2 stream and causing corrosion. The other bends in the tubing were made for ease of construction and service.

2. Reactor Section

A reactor (R-1) is included in the system to produce SO_3. When SO_3 is not desired it is bypassed. Since sulfuric acid can be formed, all components downstream of the reactor are made of stainless steel.

The reactor was constructed from a single piece of one inch diameter stainless steel tubing. It consists of two sections, each heated separately. The Preheat Section was filled with pyrex raschig rings. The Catalyst Section was filled with sulfuric acid catalyst provided by the Stauffer Chemical Company.

There are three thermocouples (TC-1, 2, and 3) in the reactor. They are placed near the entrance, exit, and between the catalyst and raschig rings. The exit thermocouple is used in conjunction with a temperature controller (TIC-1) in order to regulate reactor temperatures. The other two thermocouples are used with temperature indicator (TI-1).

Beaded heaters were used on each section. A variable transformer was used on each heater. The temperature controller switches the primary power to both transformers simultaneously.

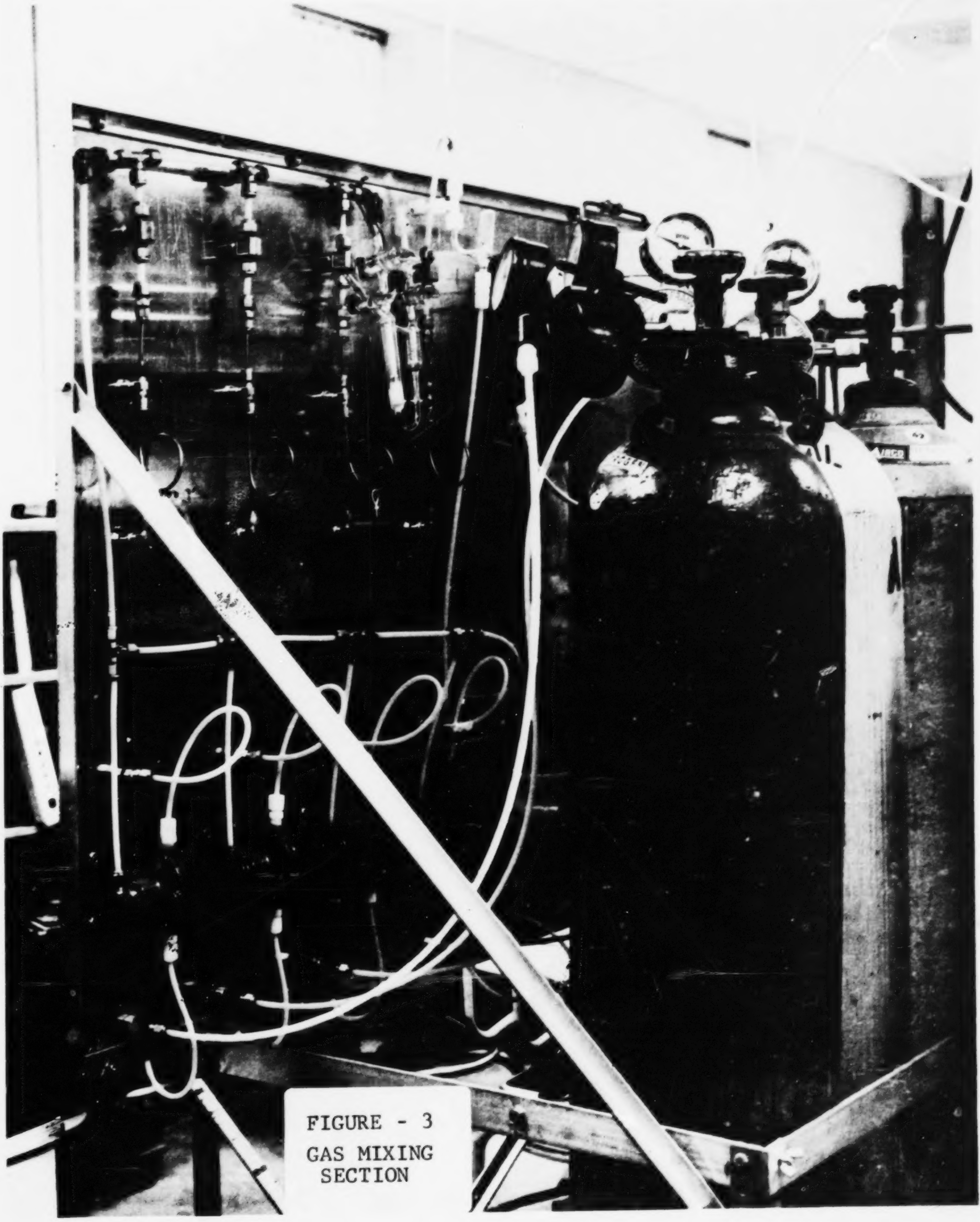


FIGURE - 3

GAS MIXING SECTION

This scheme allows the heaters to both the Preheat and the Catalyst Sections to be controlled with different voltages. In this way the two sections may be maintained at different temperatures. Operation of the Preheat Section at a higher temperature than the Reactor Section is done to take advantage of a fast reaction rate due to higher temperature at the beginning of the Catalyst Section, while at the same time obtaining a good equilibrium value due to low temperature at the exit from the Catalyst Section.

3. Pressure Control Section

The Pressure Control Section serves several purposes. First, it maintains a constant pressure in the system. This allowed the rotameters to be calibrated at a minimum number of pressures. The flow rates can thus be accurately reset. It also provides a vent for excess gas not passed through the Equipment Section.

A control valve (PCV-7) is used in conjunction with an adjustable reference pressure (PR-1). The reference pressure to the control valve is set at the desired manifold pressure. A sample port (SC-3) after the control valve is used analyze for SO_2 by Reich's test. The port was located at this point so that sample taking would not affect the system pressure or gas flow. Two toggle valves (VT-12 and 13) allow the flow to be directed into either the sample or exit line.

4. Experimental Equipment Section

Gas going to the experimental apparatus passes through the Experimental Equipment Section. The gas is first passed through a rotameter (FI-5). It is then filtered (FL-1) to remove any particulate matter from the reactor before it is allowed to enter the needle valve (VN-5). The metering valve was sized based on expected flows and a 3 psi drop. A flow controller (PCV-5) which monitors the upstream pressure is used in this stream. The control valve is referenced in this way to allow the equipment pressure to be controlled independently of the manifold pressure. A toggle valve (VT-11) downstream from the control valve is provided for quick on-off control of gas to the equipment. The pressure in the exit line from the equipment may be monitored with a mercury manometer (PI-2).

A control valve (PCV-6) of our own design was built in order to operate the equipment at various pressures. The valve may be set to control pressures over a range of one atmosphere. The valve is bypassed if the experiment is conducted at atmospheric pressure.

Figure 4 is the right half of the panel from the back. The large white object is the reactor (R-1) covered with insulation. The pressure regulator (PR-1) is visible to the left of the reactor. It is connected to the pressure control valve (PCV-7) mounted directly above the temperature indicator (TI-1). The tee above the flow controller connects to the sample line. The sample valve (VT-12) and outlet (SC-3) are in the bottom right hand corner of the photograph.

The pressure control valve farthest to the right (PCV-5) is in the Experimental Equipment Section. The filter (FL-1) mounted on the needle valve (VN-5) can be seen directly below the pressure control valve. The gas is discharged at the top of the panel.

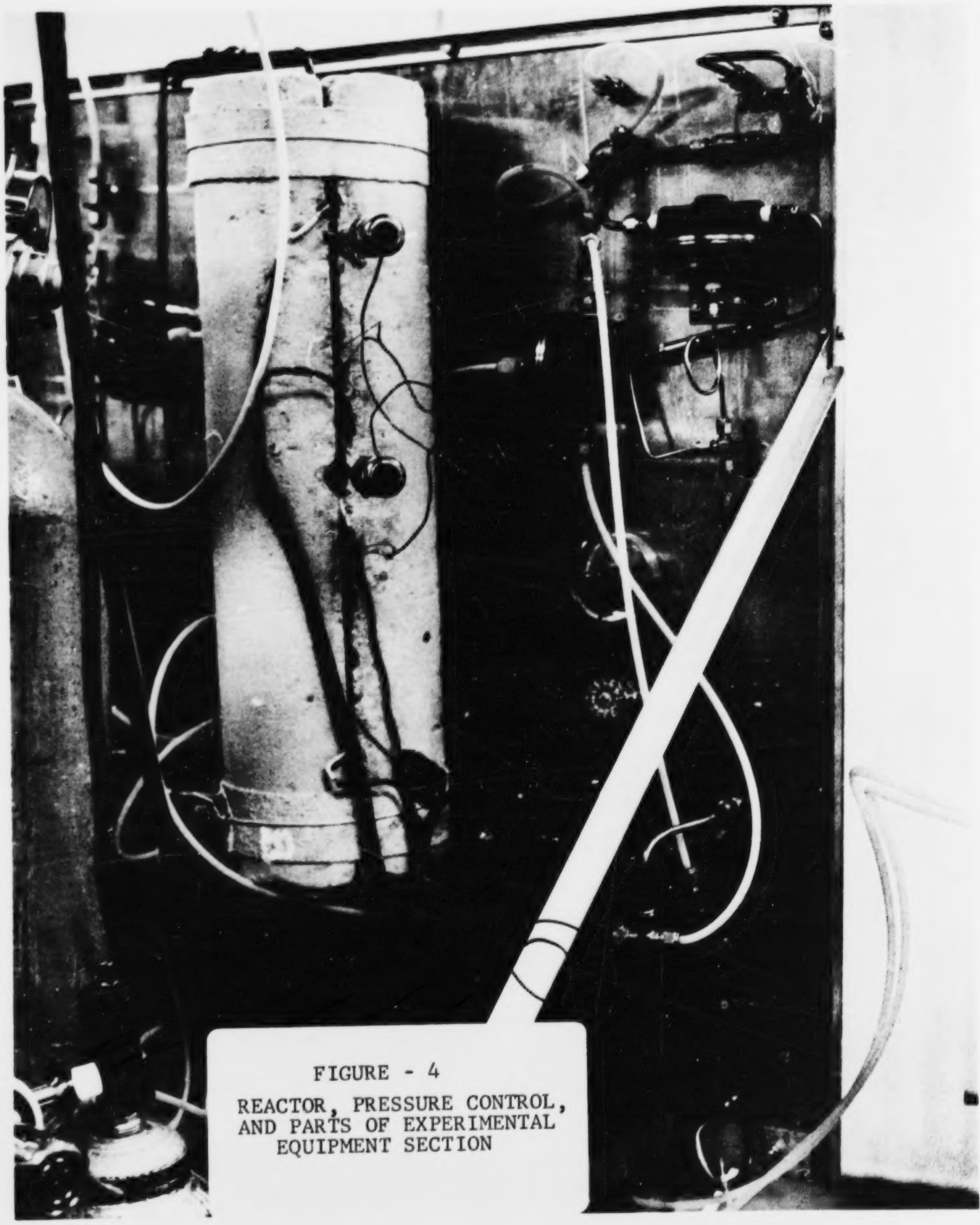


FIGURE - 4

REACTOR, PRESSURE CONTROL,
AND PARTS OF EXPERIMENTAL
EQUIPMENT SECTION

5. Scrubbing Section

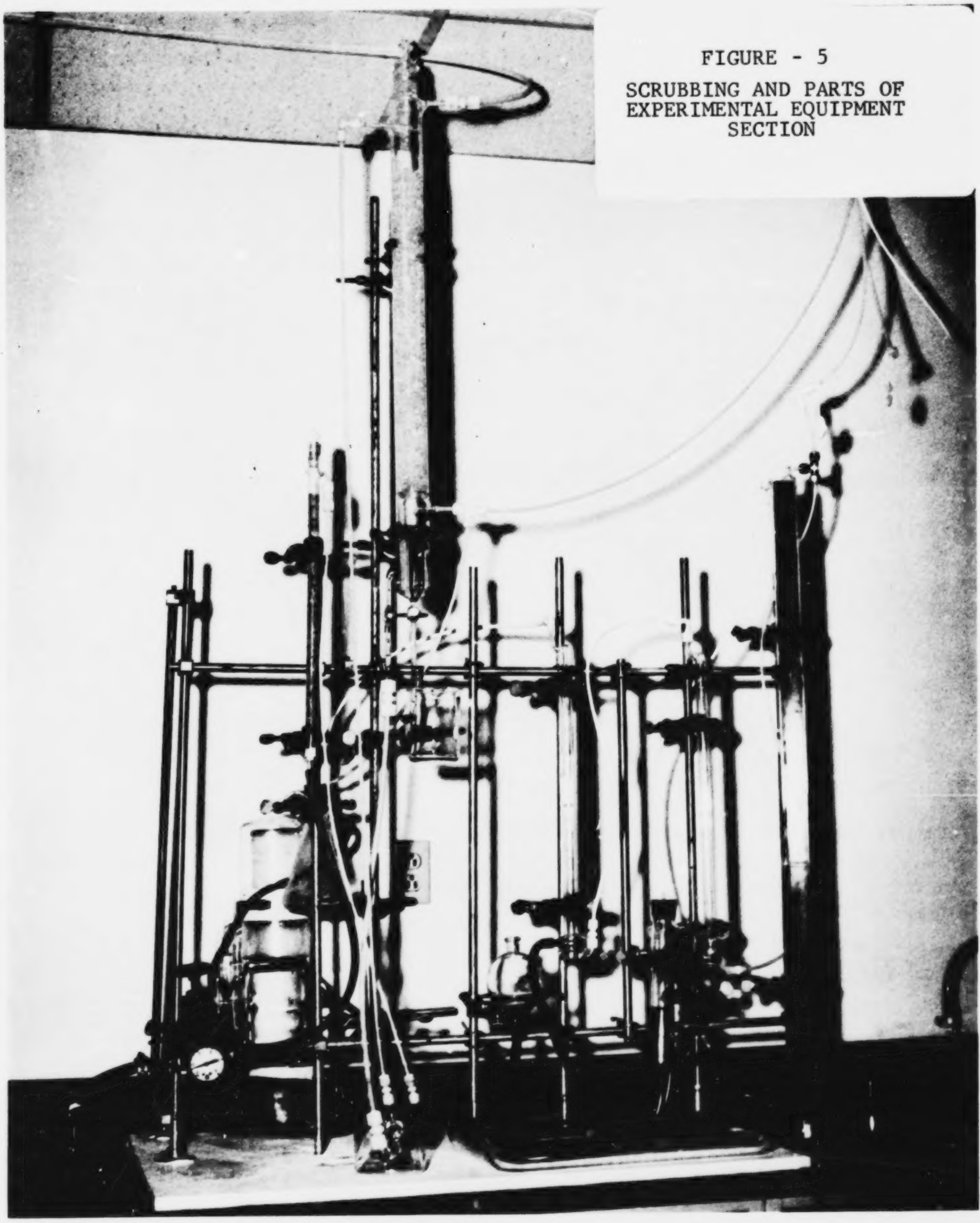
If the experiment is conducted at or above atmospheric pressure, gas from the Experimental Equipment and Pressure Control Sections is sent directly to the scrubber (S-1). The scrubber is always at atmospheric pressure. Gas entering the scrubber passes upward through raschig rings wetted with sulfuric acid before being released to the hood. The packing is kept wet by recirculating sulfuric acid collected at the bottom of the scrubber. An air lift pump (P-1) was designed to recirculate the small quantities of sulfuric acid required.

If the experiment is conducted at less than atmospheric pressure, a water aspirator (ASP-1) and gas-liquid separator (GLS-1) are used. The water aspirator serves as a vacuum pump, while at the same time it provides a convenient reference pressure for the control valve in the Experimental Equipment Section. The gas-liquid mixture from the aspirator is passed through the separator before the water is released to the drain. The gas, now at atmospheric pressure, enters the scrubber.

Figure 5 shows the Scrubbing Section as well as parts of the Experimental Equipment Section. The mercury manometer (PI-2) is at the right of the picture. The two units located above the large dish are the pressure control valves (PCV-6). Gas flowing out of the top of this valve goes to the water aspirator (ASP-1) which is located against the wall in the left hand corner. The separator (GLS-1) is located directly in front of the aspirator. Gas from the separator flows through the scrubber (S-1) before discharging to the hood through the line along the ceiling. The gas lift pump (P-1) is located in the breaker in the foreground. The pump recirculates acid collected at the bottom of the scrubber.

FIGURE - 5

SCRUBBING AND PARTS OF EXPERIMENTAL EQUIPMENT SECTION



In the design of small equipment such as this, it is often convenient to have the names of the manufacturers of critical components. This is true in this design for the control and metering valves. Hence manufacturers names have been given for critical components in Table I, the equipment list.

In summary, our gas mixing apparatus enables us to produce gas mixtures of almost any composition. Included in the system are a reactor to produce SO_3 and a scrubber to remove SO_3 before discharge into the atmosphere. Flows are reproducable and can be accurately controlled. Step changes in gas composition can be obtained without affecting the flow through the Experimental Equipment Section. Gas analysis equipment was included to provide an independent means of determining compositions.

J. P. Nolley

P S Lowell

TABLE I

LIST OF EQUIPMENT

DESIGNATION	DESCRIPTION AND MANUFACTURING TYPE	MANUFACTURER
ASP-1	Water Aspirator	---
CM-1	Cyclone Gas Mixer	*
CS-1	Cyclone Separator	*
FI-1	Flow Indicator (Rotameter), Model 622PBV, Tube Type 601	Matheson, East Rutherford, N.J.
FI-2,3,4	Flow Indicator, Model 622PBV, Tube Type 600	Matheson
FI-5	Flow Indicator, Model 622PSV, Tube Type 601	Matheson
FL-1	Filter, Series F	Nupro, Cleveland Ohio
GLS-1	Gas-Liquid Separator	*
H-1	Humidifier	*
P-1	Pump, Gas Lift	*
PCV-1,2,3,4	Pressure Control Valve, Flow Controller Model 63BDL	Moore Products, Spring House, Pa.
PCV-5,7	Pressure Control Valve, Flow Controller Model 63SUL	Moore Products
PCV-6	Pressure Control Valve (2 units)	*
PI-1	Pressure Indicator, Bourdon Tube, 0-30 psig	---
PI-2	Pressure Indicator, Mercury Manometer	*
PR-1	Pressure Regulator, Series 40	Moore Products
PSV-1,2	Pressure Safety Valve, Series R, Adjustable 10-50 psig	Nupro

* Items designed and built at TRACOR

TABLE I/LIST OF EQUIPMENT (continued)

DESIGNATION	DESCRIPTION AND MANUFACTURING TYPE	MANUFACTURER
R-1	Reactor	*
S-1	Scrubber	*
TC-1,2,3	Thermocouples	---
TI-1	Temperature Indicator	---
TIC-1	Temperature Indicating Controller, Model 2510-1 with 4000-110 Power Supply	International Instruments Inc. Orange, Conn.
VC-1	Valve, Check, Model 401X	Matheson
VN-1,2,3,4	Valve, Needle, Series S, Type B-2S	Nupro
VN-5	Valve, Needle, Series S, Type SS-2S	Nupro
VSC-1,2	Valve, Stopcock (glass)	---
VSC-3,4	Valve, Stopcock (teflon)	---
VT-1,2-10	Valve, Toggle, Series 1	Whitey Research Tool Emeryville, Calif.
VT-11,12,13	Valve, Toggle, Series 450	Hoke Manufacturing Co. Cresskill, N. J.
VTW-1	Valve, Three-Way (glass)	---

* Items Designed and built at TRACOR

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

23 May 1969 T. Parsons

TECHNICAL MEMORANDUM 004-009-Ch24

DETERMINATION OF SPECIFIC SURFACE AREA BY THE BET METHOD

TABLE OF CONTENTS

I. INTRODUCTION 1

II. THEORETICAL DISCUSSION OF THE METHOD 2

III. DATA COLLECTION 6
  A. Apparatus
  B. Calibration
  C. Procedure

IV. DATA ANALYSIS 17

V. RESULTS 21

BIBLIOGRAPHY

APPENDIX A - LISTING AND FLOW CHART OF PROGRAM SSAREA

I. INTRODUCTION

This report describes the methods and apparatus used in determining the surface areas of metal oxides. The method of preparation of a sample and the resulting physical properties affect its kinetic activity. Knowledge of the surface area of a sample is an aid in characterizing its reactivity. Samples of the same metal oxide with different surface areas differ in rate of SO_2 sorption. We assume that the greater the exposed area of sorbent, the more SO_2 molecules it can come in contact with and therefore the more SO_2 the metal oxide can sorb. Therefore, surface area determinations were an important part of the program to collect kinetic data for the SO_2 sorption reactions of metal oxides.

The specific surface of metal oxide sorbents was determined using the BET (Brunauer, Emmett, and Teller) method (BR-006). The method is well known and widely applied. It involves the measurement of the amount of gas (adsorbate) which is adsorbed on the surface of a sample (adsorbent) at a particular pressure and constant temperature.

II. THEORETICAL DISCUSSION OF THE METHOD

The BET equation is given in Equation (1).

$$\frac{p_i}{V_i(p_{o_i}-p_i)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{p_i}{p_{o_i}} \qquad (1)$$

The following definitions are necessary:

V_m	Monolayer capacity in cm^3 (N.T.P.) of adsorbate per gram adsorbent
V_i	Volume of adsorbate in cm^3 (N.T.P.) adsorbed per gram sorbent at equilibrium pressure p_i (mm Hg)
p_{o_i}	The saturation vapor pressure (mm Hg) of adsorbate at the temperature of adsorption
C	See Equation (3)
p_i/p_{o_i}	Relative pressure

Equation (1) is derived in many physical chemistry textbooks. The derivation is based on a model according to which the adsorbent is composed of many identical potential sorption sites and the adsorbate condenses on and evaporates from these sites at random. In addition, it is assumed that the adsorbate molecule is adsorbed in more than one layer of molecules on the adsorbent surface and that the number of molecules per second evaporating from one layer is equal to the number per second condensing on the next. The derivation will not be given, since Equation (1) is commonly used to determine the monolayer capacity, V_m, from the adsorption isotherm. The monolayer capacity is the amount of adsorbate contained in a one molecule thick layer covering the surface of the adsorbent.

The specific surface area S in square meters per gram is calculated from V_m using Equation (2)

$$S = \frac{V_m N A_m \times 10^{-20}}{22414} \qquad (2)$$

where V_m is the monolayer capacity in cm^3 (N.T.P.) per gram, N is Avogadro's number, and A_m is the cross-sectional area of the adsorbate molecule, 16 Å^2.

Equation (1) is used to calculate V_m and C from measurements of V_i, p_i, and p_{o_i}. The monolayer capacity V_m is used to calculate specific surface area. The value of C is an indication of the validity of using the BET equation for calculating the specific surface of a particular sample from the adsorption isotherm.

From the BET derivation, C is defined by Equation (3).

$$C = e^{(E_1 - L)/RT} \frac{\nu_2}{\nu_1} \frac{a_1}{a_2} \qquad (3)$$

The factor, ν_1, is the frequency of oscillation of the molecule normal to the sorbent surface and E_1 is the energy necessary for the molecule to condense or be adsorbed on the first layer. Therefore, $\nu_1 \; e^{-E_1/RT}$ is the number of molecules per second evaporating from a given site in the first layer. Similarly, the factor, $\nu_2 \; e^{-L/RT}$, is the number of molecules per second evaporating from or adsorbing on the second layer. L is the latent heat of condensation of the adsorbate. The assumption is made for the BET model that the necessary energy for adsorption or desorption in the second and higher layers is equal to the latent heat of condensation. The factors, a_1 and a_2, compensate for the fact that only part of the available molecules will actually be adsorbed on a potential site. According to the BET model $\frac{\nu_1}{a_1} = \frac{\nu_2}{a_2}$ so that C takes the form given in Equations (4a) and (4b).

$$C = e^{(E_1 - L)/RT} \tag{4a}$$

$$E_1 - L = RT\ln C \tag{4b}$$

The factor, E_1-L, is the "net heat of adsorption." One of the assumptions for the BET model concerning the net heat of adsorption is that E_1 is larger than L and the energy for condensation decreases from E_1 to L after the monolayer is formed. One consequence of this assumption is that C must be greater than 1 for the BET model to be satisfied and for Equation (1) to be used with validity for determining monolayer capacity from the adsorption isotherm. Values of the net heat of adsorption calculated from (4b) with T = 77°K for C varying from 1 to 1000 are shown in Table 1.

TABLE I

$K = 1.987 \times 10^{-3}$ KCAL/MOLE°K

T = 77°K

C	E_1-L (KCAL/MOLE)
1	0.
2	.011
10	0.35
100	0.70
1000	1.40

Since values of a and ν cannot be determined experimentally, the assumption that $\frac{\nu_1}{a_1} = \frac{\nu_2}{a_2}$ cannot be tested. Therefore, C is actually considered only an approximate indication of the net heat of adsorption.

The values of V_m and C are determined from Equation (1) by plotting experimentally obtained values of $\frac{p_i}{V_i(p_{o_i}-p_i)}$ vs. $\frac{p_i}{p_{o_i}}$ and finding the slope and intercept of the resulting straight line. The "normal" range of relative pressures for which the plot is actually linear and the BET equation is valid varies from about .05 to .35. Gregg and Sing (GR-002) show data by MacIver and Emmett (MA-006) for which the linear range of relative pressure is .01 to .1. The authors report that unless data are collected over the linear range the intercept may be negative which would result in a negative value of C (GR-002).

III. DATA COLLECTION

The data necessary for calculating the monolayer capacity according to Equation (1) are pressure, temperature, and volume values for a system containing sample (adsorbent) and adsorbate. The calculations were based on ideal gas behavior.

$$PV = nRT \qquad (5)$$

Since helium is not adsorbed at liquid nitrogen temperatures, the number of moles of gas n was constant during volume determinations and Equation (6) was used (see Part B, Calibration).

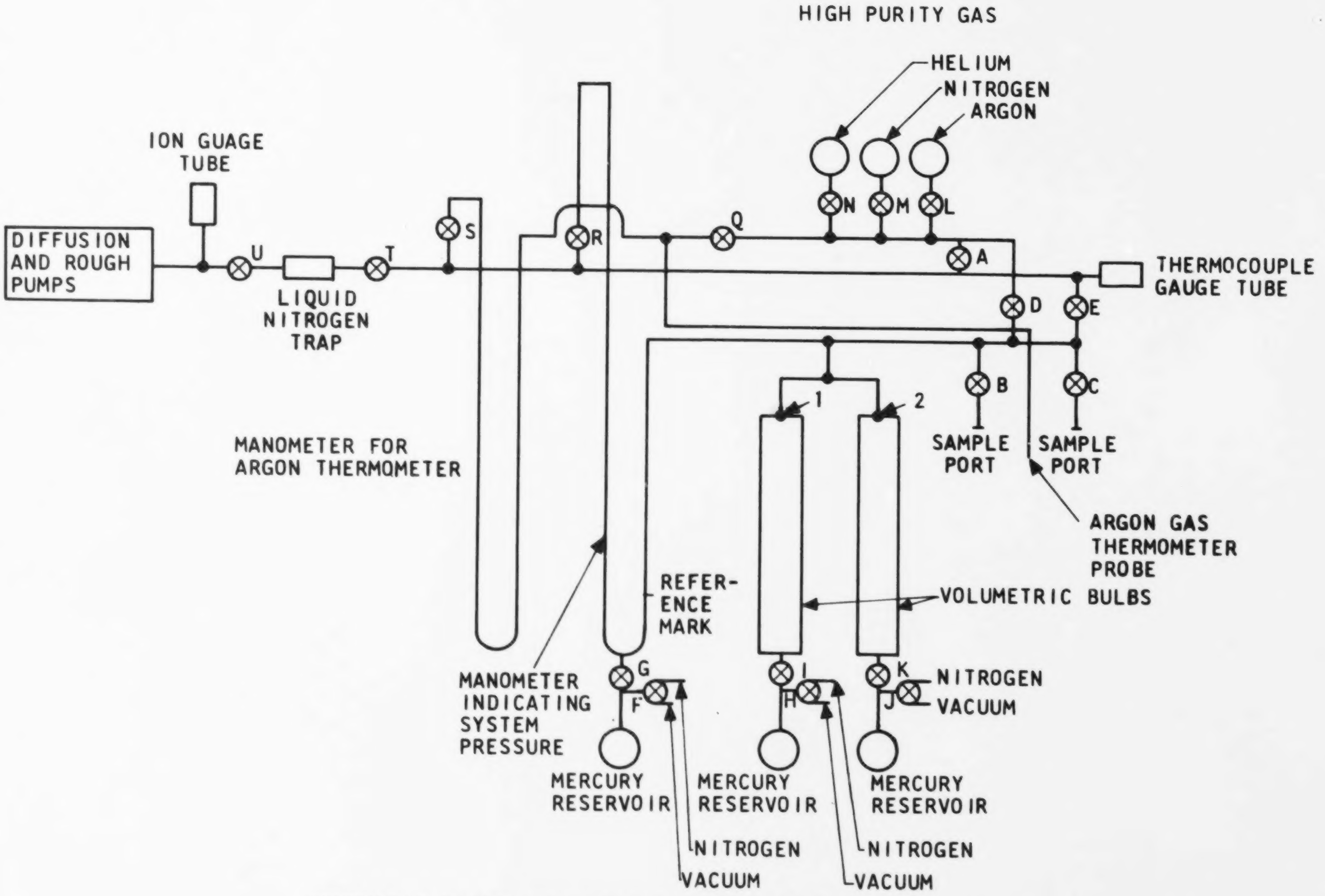
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad (6)$$

For correction of adsorbate volumes to N.T.P., Equation (7) was used where P_1 was in mm mercury and T_1 in degrees K. When two parts of the system were at different temperatures, Equation (8) was used for correction to N.T.P.

$$V_{N.T.P.} = V_1 \frac{P_1 \; (273.16)}{T_1 \; (760)} \qquad (7)$$

$$V_{N.T.P.} = \frac{V_1 \; P(273.16)}{T_1 \; (160)} + \frac{V_2 \; P(273.16)}{T_2 \; (760)} \qquad (8)$$

The general procedure followed was to introduce a known amount of gaseous adsorbate to the sample enclosed in a known volume, allow the sample to adsorb the gas until equilibrium


HIGH PURITY GAS
HELIUM
NITROGEN
ARGON
N
M
L
ION GUAGE TUBE
Q
A
DIFFUSION AND ROUGH PUMPS
U
T
S
R
THERMOCOUPLE GAUGE TUBE
LIQUID NITROGEN TRAP
D
E
B
C
1
2
SAMPLE PORT
SAMPLE PORT
MANOMETER FOR ARGON THERMOMETER
ARGON GAS THERMOMETER PROBE
REFER-ENCE MARK
VOLUMETRIC BULBS
MANOMETER INDICATING SYSTEM PRESSURE
G
F
I
H
K
J
NITROGEN
VACUUM
MERCURY RESERVOIR
MERCURY RESERVOIR
MERCURY RESERVOIR
NITROGEN
VACUUM
NITROGEN
VACUUM

SCHEMATIC DIAGRAM OF APPARATUS FOR DETERMINING SPECIFIC SURFACE AREA USING THE BET METHOD

M A6-2-1290

reference mark by adjusting the pressure over the mercury in the reservoir. The left leg of the manometer is read with the aid of a cathetometer.

Two sets of thermostated volumetric bulbs enable the operator to vary the volume of the system by known amounts. The bulbs may be filled or emptied, thereby decreasing or increasing the volume and the pressure, by adjusting the mercury level in the bulb train. This is accomplished by controlling the pressure in the mercury reservoir.

The temperature of the sample immersed in a liquid nitrogen bath is monitored with an argon gas thermometer. The argon pressure is determined with a manometer located adjacent to the system manometer. The thermometer probe is next to the sample bulb which is immersed in a liquid nitrogen bath during determinations. The sample bulbs are attached to the system by means of Cajon fittings.

All gases used (helium, nitrogen, and argon) are at least 99.999% pure (Matheson Co., LaPorte, Texas). The gases are contained in glass flasks which are blown into the system.

The system is capable of determining not only the adsorption isotherms for calculation of surface area but desorption isotherms as well for calculation of pore volume distribution.

B. Calibration

The volumes of the volumetric bulbs were determined by filling the bulbs with mercury, weighing the mercury, and dividing the weight of mercury contained in each bulb by the density of mercury at room temperature. Each weighing was carried out three times and an average value taken. The average deviation in volume calculated was .007 cm^3.

The volume of the system between the reference mark, stopcocks B, C, D and E, and points 1 and 2 in Figure 2 was designated as volume A (V_A) and was determined by admitting nitrogen to the system through stopcocks M and D with stopcocks A, B and C closed.

The pressure was determined by reading the difference in height of the manometer mercury columns with the right leg set at the reference mark (see Figure 2). Then the volume was changed a known amount by filling the volumetric bulbs with mercury with stopcock D closed, and the system pressure was again determined with the manometer set at the reference mark. Volume A was then calculated from Equation (9) where p_1 is the system pressure at

$$\frac{p_1\ (V_A + V_1)}{T_{sys}} = \frac{p_2\ (V_A + V_2)}{T_{sys}} \qquad (9)$$

the first volume (V_1), p_2 is the system pressure at the second volume (V_2), and T_{sys} is the system temperature. The least uncertainty in determining volume A occurred when the greatest change in volume and pressure took place. Volume A was determined by taking 10 measurements and calculating the average to be 19.98 ± .02 cm^3.

The same procedure was used for determing the volume between the reference mark, points 1 and 2, stopcocks C, D, E and sample port B. Then volume A was subtracted and the volume between stopcock B and the sample port, V_B, was determined to be 1.37 ± .02 cm^3. The corresponding volume, V_c, for the area from stopcock C to the rightmost sample port was also determined to be 1.37 ± .02 cm^3.

A sample whose specific surface area was determined previously in the laboratory of Dr. W. Wade at the University of Texas at Austin from the nitrogen adsorption isotherm was investigated using TRACOR BET apparatus. The value $93m^2/g$, was obtained for three different samples at TRACOR. The average value obtained using Wade's apparatus was $100m^2/g$ while individual measurements were as low as $94m^2/g$.

C. Procedure

The metal oxides were dried in a vacuum oven, and the samples to be determined were weighed by difference using a Mettler Type B6 analytical balance. The samples were weighed into sample tubes constructed so that bumping of the sample during outgassing would not cause it to be blown into other parts of the system (see Figure 3). The metal oxide was introduced through the side arm funnel which was then closed off. The samples were outgassed overnight at about 70°C until the system reached a pressure of about 10^{-6} torr.

The sample tube containing sample, when attached through the sample ports below stopcock B or C, modified the volume of the system, so that the sample tube volume had to be determined for each sample run. This was accomplished by carrying out the following steps using helium at liquid nitrogen temperature.

1. The sample tube was immersed in a liquid nitrogen bath up to a reference mark about 4 inches below the sample port.

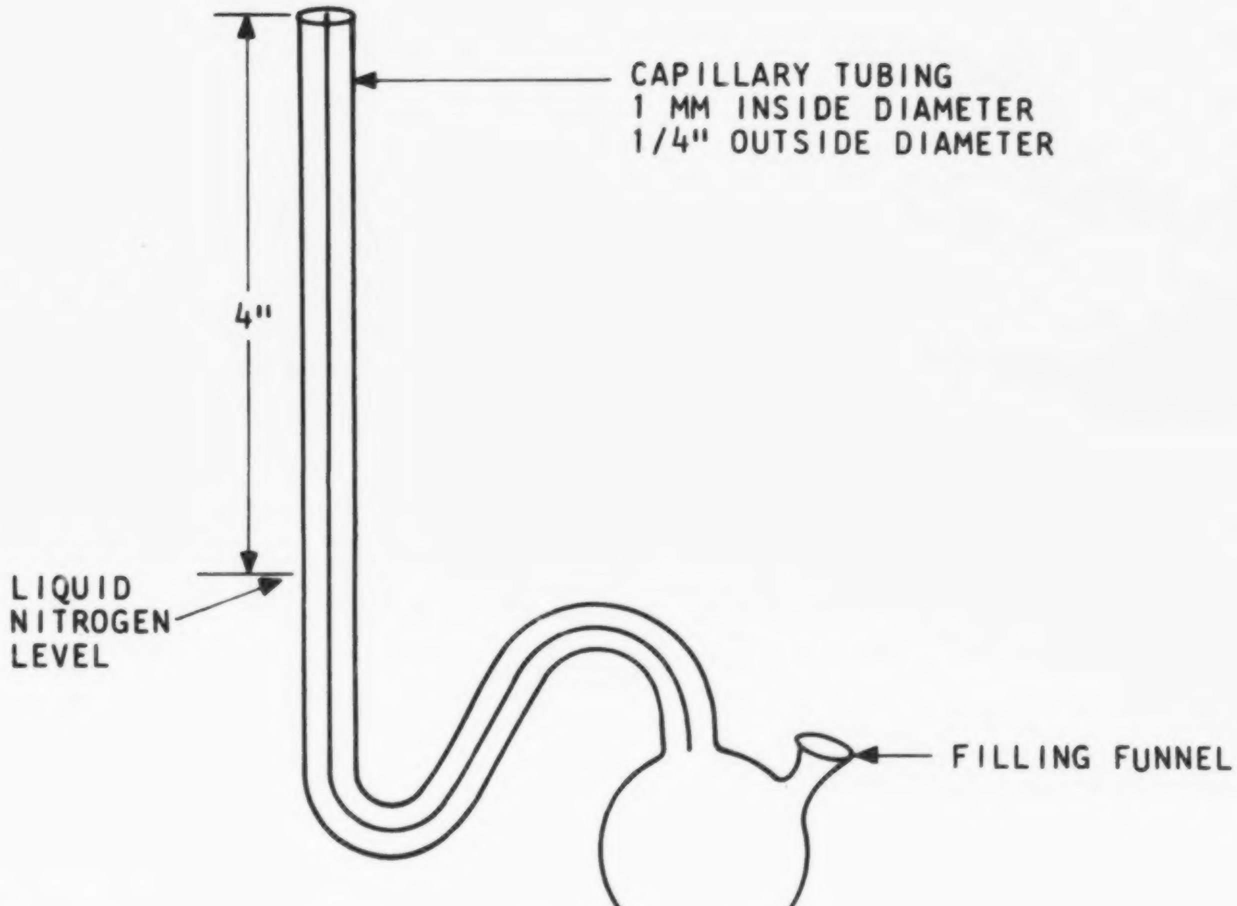

CAPILLARY TUBING
1 MM INSIDE DIAMETER
1/4" OUTSIDE DIAMETER
4"
LIQUID
NITROGEN
LEVEL
FILLING FUNNEL

FIG. 3 - SAMPLE TUBE

2. Stopcocks C, A and E were closed and stopcocks B and D were open.

3. The volumetric bulbs were emptied of mercury, and the manometer was set at the reference mark.

4. Helium was admitted to the system through stopcocks N and D which were then closed. The pressure of helium used was generally about 500 mm Hg with all the bulbs filled.

5. The manometer was again set at the reference mark and the pressure and temperature were measured.

6. The volume of the system was changed a known amount by filling some of the bulbs with mercury.

7. Pressure and temperature were measured again.

8. Changes in volume were repeated by emptying and filling the volumetric bulbs, and the pressure and temperature were again measured.

The volume of the sample tube, V_{st}, was then determined from Equation (10) where all the volumes but V_{st} had previously

$$\frac{p_1 \, (V_A + V_1 + V_B)}{T_1} + \frac{p_1 V_{st}}{T_{N_2}} = \frac{p_2 \, (V_A + V_2 + V_B)}{T_2} + \frac{p_2 V_{st}}{T_{N_2}} \qquad (10)$$

been measured. Volumes V_1 and V_2 refer to the volume in unfilled volumetric bulbs. The pressures p_1 and p_2 and temperatures T_1 and T_2 were measured directly, while T_{N_2}, the temperature of the liquid nitrogen bath in ^{o}K, was determined from the argon gas thermometer using Equations (11a) and (11b) for the vapor pressure of argon.

$$\log_{10} P = 7.5741 - 408.15/T_{N_2} \qquad (11a)$$

$$T_{N_2} = \frac{-408.15}{\log_{10}P - 7.5741} \qquad (11b)$$

In Equations (11a) and (11b) P is the difference in heights of the mercury columns in the argon thermometer in mm Hg.

The volume of the sample tube was determined several times and an average, V_{avg}, was taken.

The error, E_{vst}, was determined as described in Equation (12) where N is the number of determinations of V_{st}.

$$E_{vst} = \left[\sum_{i=i}^{N-1} (V_{avg}-V_{st_i})^2/N-1\right]^{\frac{1}{2}} \qquad (12)$$

Values of p_i, p_{o_i}, and V_i for use in Equation (1) were determined as follows. The adsorbate, nitrogen, was added to the system with the stopcock leading to the sample closed. The pressure P_{sys} (mm Hg), temperature T_{sys} (^{o}C), and volume V_{sys} of the system were measured and the original amount of adsorbate added $V_{N.T.P.}$ was calculated in cm^3 at N.T.P. from Equation (13).

$$V_{N.T.P.} = \frac{V_{sys}\ P_{sys}\ (273.16)}{(T_{sys} + 273.16)(760)} \qquad (13)$$

Generally about 100 mm of adsorbate were added with half the volumetric bulbs filled with mercury.

Next, with all the bulbs empty, the sample stopcock was opened, the manometer was set to the reference mark, and the sample was allowed to adsorb nitrogen until equilibrium was reached or for about 15 minutes. The following data were then taken for the first point:

1. System pressure p_i in mm Hg
2. Volume of bulbs unfilled with mercury for calculating volume of the system V_{sys_i}
3. System temperature T_i in ^oC
4. Argon pressure in gas thermometer for calculating temperature of the liquid nitrogen bath $T_{N_2\,i}$ from Equation (11b)

From these data the volume of adsorbate V_{ads_i} present in the system at equilibrium pressure p_i recalculated to N.T.P. was determined using Equation (14).

$$V_{ads_i} = \frac{V_{sys_i}\, p_i\, (273.16)}{(T_i + 273.16)(760)} + \frac{V_{st}\,(1-\alpha p_i) p_i\, (273.16)}{T_{N_2\,i}\,(760)} \qquad (14)$$

The volume V_{sys_i} is the part of the volume of the system at "room" temperature and is determined from Equation (15).

$$V_{sys_i} = V_A + V_B \text{ (or } V_C) + V_{bulbs} + .047 \qquad (15)$$

Either V_B or V_C is used, depending on through which sample port the sample bulb is introduced. V_{bulbs} is the volume of the empty volumetric bulbs. The constant .047 is a correction for the amount of sample tube volume which is not at liquid nitrogen temperature (about 4 inches of 1 mm capillary tubing). The factor $(1-\alpha p_i)$ in Equation (15) is a correction for non-ideality of the adsorbate. For nitrogen, α is 6.6×10^{-5}.

By subtracting V_{ads_i}, the amount of adsorbate present at p_i, from $V_{N.T.P.}$, the amount of adsorbate added before sorption, one can determine the amount adsorbed at pressure p_i. Dividing by the sample weight in grams gives the factor V_i necessary for Equation (1).

The process described above was repeated by filling each of the volumetric bulbs with mercury, thereby increasing the pressure, allowing the adsorbent to come to equilibrium, and recording the pressure, temperature and volume.

The quantity p_{o_i}, was calculated using Equation (16) for the vapor pressure of nitrogen.

$$\log p_{o_i} = 6.866 - \frac{308.365}{T_{N_2 i}} \qquad (16)$$

The factor $T_{N_2 i}$ was calculated from argon thermometer data for temperature of the liquid nitrogen bath (Equation 11b).

IV. DATA ANALYSIS

The calculations for determining V_i, p_i, and p_{o_i} for each run have been described in Part III, Data Collection. These data are used in Equation (1) which is the equation for a straight

$$\frac{p_i}{V_i(p_{o_i}-p_i)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\frac{p_i}{p_{o_i}} \tag{1}$$

line with slope $\frac{C-1}{V_mC}$ and intercept $\frac{1}{V_mC}$. A computer program, SSAREA, was written at TRACOR to calculate V_i, p_i, p_{o_i} from input pressure, temperature, and volume data using Equations (14) and (16) and to find the best straight line with ordinate $y_i = \frac{p_i}{V_i(p_{o_i}-p_i)}$ and abscissa $x_i = \frac{p_i}{p_o}$. Substituting x_i and y_i in (1) gives Equation (17)

$$y_i = \frac{1}{V_mC} + \frac{C-1}{V_mC}x_i \tag{17}$$

The input data are in the form of heights of left and right manometer columns, numbers of volumetric bulbs filled with mercury, and temperature in degrees C. It is unnecessary for the operator to perform any calculations since known system volumes and constants such as vapor pressure equation coefficients are stored by the program. A program listing of SSAREA is given in Appendix A. The program determines the slope and intercept of the least squares regression line of best fit from Equations (22) and (23), respectively. The error to be minimized, E_i, is given in Equation (18) where the slope m is $\frac{C-1}{V_mC}$ and the intercept b is $\frac{1}{V_mC}$.

$$E_i = mx_i + b - y_i \tag{18}$$

The sum of the squared error, S, is given in Equation (19).

$$S = \sum_{i=1}^{n} E_i^2 = \sum_{i=1}^{n} (mx_i + b - y_i)^2 \tag{19}$$

The conditions for a minimum are:

$$\frac{\partial S}{\partial m} = 2\sum_{i=1}^{n} (mx_i + b - y_i)(x_i) = 0 \tag{20}$$

$$\frac{\partial S}{\partial b} = 2\sum_{i=1}^{n} (mx_i + b - y_i) = 0 \tag{21}$$

Rearranging and solving for m and b gives:

$$m = \frac{\Sigma\, x_i y_i - \frac{1}{n}\Sigma\, x_i\, \Sigma\, y_i}{\Sigma\, x_i^2 - \frac{1}{n}(\Sigma\, x_i)^2} \tag{22}$$

$$b = \frac{\Sigma\, x_i y_i\, \Sigma\, x_i - \Sigma\, x_i^2\, \Sigma\, y_i}{(\Sigma\, x_i)^2 - n\, \Sigma\, x_i^2} \tag{23}$$

Solving for V_m and C gives Equations (24) and (25) which can be

$$V_m = \frac{1}{m + b} \tag{24}$$

$$C = \frac{m}{b} + 1 \qquad (25)$$

solved using Equations (22) and (23).

The error E_v between calculated and observed values of V_i is determined according to Equation (26) and printed as the "RMS error for volume adsorbed."

$$E_v = \left[\frac{\sum_{i=1}^{n} (V_i - V_{i_{calc}})^2}{n} \right]^{\frac{1}{2}} \qquad (26)$$

The calculated V_i is given in Equation (27).

$$V_{i_{calc}} = \frac{\dfrac{p_i}{p_{o_i} - p_i}}{m \dfrac{p_i}{p_{o_i}} + b} \qquad (27)$$

The error between calculated and observed values of y_i is given in Equation (28), and the calculated y_i is given in Equation (29).

$$E_y = \left[\frac{\sum_{i=1}^{n} (y_i - y_{i_{calc}})^2}{n} \right]^{\frac{1}{2}} \qquad (28)$$

$$y_{i_{calc}} = m \frac{p_i}{p_{o_i}} + b \qquad (29)$$

The error E_y is printed as the "correlation error for $\frac{p}{V(p_o - p)}$." Errors in the slope and intercept are given by Equations (30) and (31) and are also printed.

$$E_m = \left[\frac{1}{\sum_{i=1}^{n} x_i^2 - N\left(\sum_{i=1}^{n} x_i\right)^2} \right]^{\frac{1}{2}} E_y \qquad (30)$$

$$E_b = \left[\frac{\sum_{i=1}^{n} x_i}{N\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2} \right]^{\frac{1}{2}} E_y \qquad (31)$$

From Equation (24) the probable error in V_m is given by

$$\begin{aligned} \Delta V_m^2 &= \left(E_m \frac{\partial V_m}{\partial m}\right)^2 + \left(E_b \frac{\partial V_m}{\partial b}\right)^2 \\ &= E_m^2 \left(\frac{1}{m + b}\right)^2 + E_b^2 \left(\frac{1}{m + b}\right)^2 \end{aligned} \qquad (32)$$

Therefore, the error in V_m can be calculated knowing E_m and E_b from:

$$E_{vm} = \left[\frac{E_m^2 + E_b^2}{(m + b)^2} \right]^{\frac{1}{2}} \qquad (33)$$

The error E_{vm} is printed as the "error in specific surface area."

V. RESULTS

Examples of the results obtained are given on the following pages.

```
PAGE    4                                                                                   16  APR  1969
                    DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

     SAMPLE DESCRIPTION                                    ZRO2 634-63-1
                                                  170-325 MESH, OUT GASSED AT 65C

                        B E T EQUATION:    P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

       SAMPLE              REDUCED           VOLUME ADSORBED PER GRAM             P/V(PO-P)               NORMALIZED
     TEMPERATURE        PRESSURE P/PO             SAMPLE AT STP                     (G/ML)                 WEIGHTING
     (DEG. K)             (MM HG)                    (ML/G)                                                 FUNCTION

                                            OBSERVED    CALCULATED          OBSERVED    CALCULATED
        77.6                .046              1.006       1.040              .04816      .04660              1.00
        77.5                .059              1.047       1.061              .05944      .05867              1.00
        77.4                .080              1.073       1.092              .08093      .07947              1.00
        77.4                .101              1.117       1.123              .10082      .10028              1.00
        77.5                .127              1.160       1.159              .12496      .12512              1.00
        77.4                .149              1.207       1.192              .14532      .14723              1.00
        77.4                .200              1.300       1.270              .19174      .19638              1.00
        77.4                .224              1.330       1.310              .21645      .21978              1.00
        77.4                .265              1.393       1.386              .25925      .26061              1.00
        77.4                .279              1.406       1.412              .27516      .27393              1.00
        77.4                .292              1.411       1.440              .29288      .28705              1.00

              VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =    1.02  ML/G

                RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  677.24

     CORRELATION ERROR FOR P/V(PO-P) =  .00268          C-1/VM*C =   .9768            1/VM*C =  .00144

          RMS ERROR FOR VOLUME ADSORBED =      .02                    ERROR IN C-1/VM*C =    .0093

               ERROR IN 1/VM*C =    .00175                          ERROR IN VM =      .01

                                 SPECIFIC SURFACE AREA =    4.35 * VM

                          SPECIFIC SURFACE AREA =    4.45  SQUARE METERS/GRAM

                              ERROR IN SPECIFIC SURFACE AREA =     .04
```

```
PAGE    4                                                                              11  APR  1969
                  DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

     SAMPLE DESCRIPTION                                    NIO 634-65-2
                                                 170-325 MESH, OUT GASSED  75 C

                        B E T EQUATION:    P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

     SAMPLE          REDUCED       VOLUME ADSORBED PER GRAM              P/V(PO-P)            NORMALIZED
   TEMPERATURE     PRESSURE P/PO       SAMPLE AT STP                      (G/ML)               WEIGHTING
    (DEG. K)         (MM HG)              (ML/G)                                               FUNCTION

                                   OBSERVED    CALCULATED          OBSERVED   CALCULATED
      77.5            .032          12.735       12.327             .00261      .00270           1.00
      77.5            .040          13.176       12.887             .00315      .00322           1.00
      77.5            .054          13.536       13.637             .00419      .00417           1.00
      77.5            .064          13.943       14.055             .00490      .00486           1.00
      77.5            .085          14.591       14.755             .00636      .00629           1.00
      77.5            .108          15.216       15.400             .00794      .00785           1.00
      77.5            .131          15.903       15.997             .00949      .00944           1.00
      77.5            .152          16.495       16.510             .01085      .01085           1.00
      77.5            .172          17.096       17.013             .01218      .01224           1.00
      77.5            .181          17.318       17.225             .01275      .01283           1.00

            VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =   14.58  ML/G

              RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  135.20

     CORRELATION ERROR FOR P/V(PO-P) =  .00006          C-1/VM*C =   .0681          1/VM*C =  .00051

          RMS ERROR FOR VOLUME ADSORBED =     .19                  ERROR IN C-1/VM*C =    .0004

               ERROR IN 1/VM*C =   .00004                     ERROR IN VM =      .08

                              SPECIFIC SURFACE AREA =    4.35 * VM

                     SPECIFIC SURFACE AREA =   63.44  SQUARE METERS/GRAM

                         ERROR IN SPECIFIC SURFACE AREA =     .35
```

```
PAGE    4                                                                                 18  APR  1969
                     DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

  SAMPLE DESCRIPTION                                    SB205 634-67-1
                                               170-325 MESH, OUT GASSED AT 65C

                     B E T EQUATION:    P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

    SAMPLE           REDUCED         VOLUME ADSORBED PER GRAM               P/V(PO-P)                NORMALIZED
  TEMPERATURE     PRESSURE P/PO         SAMPLE AT STP                        (G/ML)                  WEIGHTING
   (DEG. K)          (MM HG)               (ML/G)                                                    FUNCTION

                                    OBSERVED    CALCULATED          OBSERVED    CALCULATED
      77.4             .040           3.972        3.978              .01061       .01060               1.00
      77.4             .051           4.142        4.093              .01286       .01299               1.00
      77.4             .069           4.327        4.268              .01711       .01734               1.00
      77.4             .083           4.325        4.415              .02240       .02194               1.00
      77.3             .112           4.554        4.579              .02775       .02760               1.00
      77.3             .132           4.684        4.709              .03245       .03227               1.00
      77.3             .179           5.070        5.019              .04297       .04340               1.00
      77.3             .202           5.211        5.178              .04854       .04885               1.00
      77.3             .243           5.472        5.479              .05870       .05862               1.00
      77.3             .256           5.577        5.582              .06185       .06178               1.00
      77.3             .270           5.673        5.699              .06510       .06492               1.00

              VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =    4.20  ML/G

                RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  235.34

     CORRELATION ERROR FOR P/V(PO-P) =  .00025         C-1/VM*C =   .2370          1/VM*C =  .00101

         RMS ERROR FOR VOLUME ADSORBED =      .04                  ERROR IN C-1/VM*C =     .0009

             ERROR IN 1/VM*C =    .00016                     ERROR IN VM =       .02

                             SPECIFIC SURFACE AREA =    4.35 * VM

                        SPECIFIC SURFACE AREA =   18.28  SQUARE METERS/GRAM

                             ERROR IN SPECIFIC SURFACE AREA =     .07
```

```
PAGE    4                                                                                  11  MAR  196
                        DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

   SAMPLE DESCRIPTION                                    AL203 634-53-A
                                                  170-325 MESH,DE-GASSED 110C

                        B E T EQUATION:    P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

   SAMPLE          REDUCED        VOLUME ADSORBED PER GRAM            P/V(PO-P)              NORMALIZED
 TEMPERATURE     PRESSURE P/PO       SAMPLE AT STP                     (G/ML)                 WEIGHTING
 (DEG. K)         (MM HG)               (ML/G)                                                FUNCTION

                                  OBSERVED    CALCULATED         OBSERVED   CALCULATED
     77.3            .008          49.872        47.285            .00017      .00018              1.00
     77.3            .011          51.724        51.160            .00021      .00021              1.00
     77.3            .012          53.050        53.868            .00024      .00023              1.00
     77.3            .015          54.704        57.268            .00029      .00027              1.00
     77.3            .084          72.992        76.792            .00126      .00119              1.00
     77.3            .099          75.645        78.785            .00146      .00140              1.00
     77.3            .124          79.540        81.723            .00177      .00173              1.00
     77.3            .139          81.840        83.530            .00198      .00194              1.00
     77.3            .167          85.774        86.866            .00234      .00231              1.00
     77.3            .183          87.804        88.798            .00255      .00253              1.00
     83.3            .121          96.998        81.417            .00142      .00169              1.00

             VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =    74.13  ML/G

                RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  202.58

      CORRELATION ERROR FOR P/V(PO-P) =  .00009         C-1/VM*C =   .0134          1/VM*C =  .00007

         RMS ERROR FOR VOLUME ADSORBED =     5.15                   ERROR IN C-1/VM*C =     .0004

             ERROR IN 1/VM*C =   .00005                         ERROR IN VM =     2.35

                                 SPECIFIC SURFACE AREA =    4.35 * VM

                         SPECIFIC SURFACE AREA =  322.54  SQUARE METERS/GRAM

                              ERROR IN SPECIFIC SURFACE AREA =   10.22
```

```
PAGE    4                                                                                  10  MAR. 1969
                          DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

     SAMPLE DESCRIPTION                                         CEO2 634-37-A
                                                                OUT-GASSED AT 65

                          B E T EQUATION:     P/V(PO-P) = ((C-1)/VM.C)P/PO + 1/VM.C

     SAMPLE          REDUCED         VOLUME ADSORBED PER GRAM            P/V(PO-P)              NORMALIZED
   TEMPERATURE    PRESSURE P/PO           SAMPLE AT STP                   (G/ML)                 WEIGHTING
   (DEG. K)         (MM HG)                  (ML/G)                                               FUNCTION

                                     OBSERVED    CALCULATED         OBSERVED    CALCULATED
      77.4             .006           31.440        31.333           .00019       .00019              1.00
      77.4             .007           32.274        33.060           .00022       .00022              1.00
      77.4             .008           32.857        34.188           .00025       .00024              1.00
      77.4             .009           33.583        35.340           .00026       .00027              1.00
      77.4             .107           48.470        48.564           .00247       .00247              1.00
      77.4             .128           50.100        49.897           .00292       .00293              1.00
      77.4             .161           52.530        52.064           .00364       .00367              1.00
      77.4             .182           54.032        53.537           .00412       .00416              1.00
      77.4             .221           56.540        56.373           .00503       .00505              1.00
      77.4             .244           57.928        58.127           .00558       .00556              1.00
      77.4             .257           58.681        59.134           .00588       .00584              1.00

              VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =   44.28  ML/G

                RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  396.87

      CORRELATION ERROR FOR P/V(PO-P) =  .00002         C-1/VM.C =   .0225          1/VM.C =  .00006

          RMS ERROR FOR VOLUME ADSORBED =      .76                   ERROR IN C-1/VM.C =    .0001

               ERROR IN 1/VM.C =   .00001                       ERROR IN VM =       .14

                             SPECIFIC SURFACE AREA =    4.35 . VM

                        SPECIFIC SURFACE AREA =  192.66  SQUARE METERS/GRAM

                            ERROR IN SPECIFIC SURFACE AREA =     .62
```

```
'AGE    4                                                                                              10  MAR  1969
                              DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

     SAMPLE DESCRIPTION                                              FE2O3 634-45-A
                                                           170-325 MESH, DE-GASSED AT 70 C

                           B E T EQUATION:     P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

     SAMPLE            REDUCED          VOLUME ADSORBED PER GRAM           P/V(PO-P)                 NORMALIZED
   TEMPERATURE       PRESSURE P/PO           SAMPLE AT STP                  (G/ML)                    WEIGHTING
   (DEG. K)            (MM HG)                  (ML/G)                                                 FUNCTION

                                         OBSERVED    CALCULATED       OBSERVED    CALCULATED
      77.4               .011             37.807       34.339          .00030       .00033              1.00
      77.4               .015             39.182       37.590          .00038       .00039              1.00
      77.4               .018             40.242       39.886          .00045       .00046              1.00
      77.4               .023             41.785       42.519          .00057       .00056              1.00
      77.4               .118             55.791       56.252          .00239       .00237              1.00
      77.4               .142             57.369       58.306          .00288       .00283              1.00
      77.4               .156             58.923       59.513          .00313       .00310              1.00
      77.4               .170             60.552       60.731          .00339       .00338              1.00
      77.4               .224             66.516       65.512          .00435       .00442              1.00

                  VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) =   51.84  ML/G

                   RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) =  169.51

     CORRELATION ERROR FOR P/V(PO-P) =  .00003          C-1/VM*C =   .0192          1/VM*C =  .00011

          RMS ERROR FOR VOLUME ADSORBED =    1.40                  ERROR IN C-1/VM*C =    .0001

               ERROR IN 1/VM*C =   .00002                     ERROR IN VM =      .38

                                   SPECIFIC SURFACE AREA =    4.35 * VM

                             SPECIFIC SURFACE AREA =  225.56  SQUARE METERS/GRAM

                                 ERROR IN SPECIFIC SURFACE AREA =    1.64
```

DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

SAMPLE DESCRIPTION — CUO SAMPLE 634-47-1
170-325 MESH

B E T EQUATION: P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

SAMPLE TEMPERATURE (DEG. K)	REDUCED PRESSURE P/PO (MM HG)	VOLUME ADSORBED PER GRAM SAMPLE AT STP (ML/G)		P/V(PO-P) (G/ML)		NORMALIZED WEIGHTING FUNCTION
		OBSERVED	CALCULATED	OBSERVED	CALCULATED	
77.4	.045	11.946	12.364	.00393	.00379	1.00
77.4	.056	12.216	12.536	.00481	.00469	1.00
77.4	.068	13.943	12.734	.00524	.00576	1.00
77.4	.084	12.669	12.979	.00728	.00710	1.00
77.4	.108	13.178	13.334	.00914	.00903	1.00
77.4	.122	13.472	13.561	.01030	.01023	1.00
77.4	.152	14.115	14.063	.01274	.01278	1.00
77.4	.170	14.455	14.374	.01421	.01429	1.00
77.4	.187	14.740	14.676	.01562	.01569	1.00
77.4	.194	14.764	14.809	.01635	.01630	1.00
77.4	.201	14.872	14.927	.01688	.01682	1.00

VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) = 11.96 ML/G

RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) = 1685.52

CORRELATION ERROR FOR P/V(PO-P) = .00013　　C-1/VM*C = .0836　　1/VM*C = .00005

RMS ERROR FOR VOLUME ADSORBED = .43　　ERROR IN C-1/VM*C = .0010

ERROR IN 1/VM*C = .00014　　ERROR IN VM = .14

SPECIFIC SURFACE AREA = 4.35 * VM

SPECIFIC SURFACE AREA = 52.04 SQUARE METERS/GRAM

ERROR IN SPECIFIC SURFACE AREA = .63

DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T METHOD

SAMPLE DESCRIPTION

CR203 634-59-1
OUTGASSED AT 65C, 170-325 MESH

B E T EQUATION: P/V(PO-P) = ((C-1)/VM*C)P/PO + 1/VM*C

SAMPLE TEMPERATURE (DEG. K)	REDUCED PRESSURE P/PO (MM HG)	VOLUME ADSORBED PER GRAM SAMPLE AT STP (ML/G)		P/V(PO-P) (G/ML)		NORMALIZED WEIGHTING FUNCTION
		OBSERVED	CALCULATED	OBSERVED	CALCULATED	
77.5	.029	14.098	13.578	.00214	.00222	1.00
77.5	.036	14.392	14.066	.00262	.00268	1.00
77.4	.050	14.469	14.737	.00362	.00356	1.00
77.4	.062	15.079	15.206	.00442	.00438	1.00
77.4	.073	15.594	15.695	.00545	.00541	1.00
77.4	.099	16.175	16.259	.00681	.00677	1.00
77.4	.121	16.757	16.801	.00823	.00819	1.00
77.4	.135	17.104	17.133	.00909	.00908	1.00
77.4	.159	17.743	17.716	.01063	.01064	1.00
77.4	.166	17.953	17.903	.01111	.01114	1.00
77.4	.174	18.146	18.090	.01160	.01163	1.00

VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYER (VM) = 15.29 ML/G

RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER LAYERS (C) = 207.36

CORRELATION ERROR FOR P/V(PO-P) = .00005 C-1/VM*C = .0651 1/VM*C = .00032

RMS ERROR FOR VOLUME ADSORBED = .21 ERROR IN C-1/VM*C = .0003

ERROR IN 1/VM*C = .00003 ERROR IN VM = .06

SPECIFIC SURFACE AREA = 4.35 * VM

SPECIFIC SURFACE AREA = 66.52 SQUARE METERS/GRAM

ERROR IN SPECIFIC SURFACE AREA = .28

BIBLIOGRAPHY

BR-005 S. BRUNAUER, P.H. EMMETT, T. TELLER, J. AM. CHEM. SOC., VOL. 60, P. 309 (1938).

GR-002 S. J. GREGG, K. S. W. SINS, ADSORPTION, SURFACE AREA AND POROSITY, ACADEMIC PRESS, NEW YORK (1967)

MA-006 D. S. MACIVER, P. H. EMMETT, J. AM. CHEM. SOC., VOL. 60, P. 824 (1938).

APPENDIX A

LISTING OF PROGRAM SSAREA

```
C•••• THIS PROGRAM CALCULATES THE SPECIFIC SURFACE AREA OF A SAMPLE
C••••     FROM MEASUREMENTS OF THE VOLUME NITROGEN THE SAMPLE CAN ADSORB
C••••     AT A KNOWN TEMPERATURE. THE BET EQUATION IS USED.
C••••
C•••• HEAD - ARRAY CONTAINING HEADING TITLES
C•••• IV - FIELD DATA FLAG TO DENOTE VOLUME A OR VOLUME B
C••••      IV = VB, VOLUME B
C••••      IV = VC, VOLUME C
C•••• WS - WEIGHT OF SAMPLE (GM)
C•••• NASB - FIELD DATA FLAG USED TO DETERMINE TYPE OF ADSORBATE USED
C••••
C••••        NASB = N2, NITROGEN
C••••        NASB = KR, KRYPTON
C•••• NGAS - FIELD DATA FLAG USED TO DETERMINE TYPE OF GAS USED IN THE
C••••        THERMOMETER.
C••••        NGAS = AR, ARGON
C••••        NGAS = N2, NITROGEN
C••••        NGAS = KR, KRYPTON
C•••• NPOINT - NUMBER OF DATA POINTS IN SAMPLE RUN (GE.5 ,LE.12)
C•••• ADSORB - ARRAY OF ADSORBATE DATA
C••••           ROW 1 - NITROGEN
C••••           ROW 2 - KRYPTON
C••••           COL 1 - MOLECULAR WEIGHT
C••••           COL 2 - ALPHA COEF.
C••••           COL 3 - AREA OF MOLECULE
C•••• GAS - ARRAY OF GAS DATA USED IN THERMOMETER
C••••           ROW 1 - NITROGEN
C••••           ROW 2 - KRYPTON
C••••           ROW 3 - ARGON
C••••           COL 1 - A
C••••           COL 2 - B
C••••           COL 3 - C
C•••• IWEIGH - FLAG DENOTES WHETHER TO WEIGHT LEAST SQUARES ERROR OR NOT
C••••     IWEIGH = NO, DO NOT WEIGHT  (WEIGHT =1.0)
```

```
C****      IWEIGH = YES, CALCULATE WEIGHTS
C**** M - MOLECULAR WEIGHT OF CHOSEN ADSORBATE
C**** AM - AREA OF MOLECULE OF CHOSEN ADSORBATE (CM**2)
C**** ALPHA - ALPHA COEFFICIENT OF CHOSEN ADSORBATE
C**** VBC - VOLUME OF VB OR VC (DETERMINED BY IV)
C**** VOLA = VOLUME FROM TOP OF HG BULBS TO STOP COCKS WHICH LEAD TO SAMPLE
C****      HOLDERS TO THE STOP COCKS WHICH CONNECT TO MAIN VACUUM LINE
C**** ADSORBATE - GAS THAT IS ADSORBED BY SAMPLE
C**** GAS - GAS USED IN GAS THERMO.
C**** AG,BG,CG,AS,BS,CS - COEFFICIENTS FOR VAPOR PRESSURE EQUATIONS
C**** VOLT - TOTAL VOLUME OF SYSTEM (CC)
C**** VOL(I) - VOLUME OF I-TH BULB OF SYSTEM (CC)
C**** VOLB - VOLUME FROM LEFT MOST STOP COCK TO BRASS FITTING WHICH CONNECTS
C****      SAMPLE HOLDER.
C**** VOLC - VOLUME FROM RIGHT MOST STOP COCK TO BRASS FITTING WHICH CONNECTS
C****      SAMPLE HOLDER.
C**** P2L,P2R - MANOMETER HEIGHTS IN MM HG WHEN HELIUM IS ADDED TO SYSTEM WITH
C****      SAMPLE TUBE STOP COCK OPEN
C**** MV2,NV2 - NO. OF BULBS FILLED WHEN P2L,P2R IS READ.
C**** PGTL,PGTR - MANOMETER HEIGHTS OF GAS THERMO. TAKEN AT TIME OF VST
C****      MEASUREMENTS
C**** TRVST - ROOM TEMP (C.) WHEN PGTL,PGTR IS READ
C**** PAL,PAR,NA,MA,TRA - TAKEN WITH SAMPLE STOP COCK CLOSED AND ORIGINAL
C****      AMOUNT OF ADSORBATE IN SYSTEM BEFORE ANY ADSORBATE HAS BEEN INTRO.
C****      DUCED TO SAMPLE
C**** PL,PR - MANOMETER HEIGHTS OF SUFFICIENT DIFF. TO MEASURE AN ACCURATE
C****      PRESSURE OF ADSORBATE AFTER THE SAMPLE HAS BEEN EXPOSED TO THE
C****      ADSORBATE. THE PRESSURE MEASUREMENTS ARE VALID FOR THE VOLUME AS
C****      INDICATED BY NTM,MTM. THEY MAY OR MAY NOT BE INDICATIVE OF THE PRESS.
C****      WHEN SAMPLE IS AT EQUILB.
C**** NTM,MTM - VOLUMES OF FILLED BULBS WHEN PL,PR ARE TAKEN. MAY OR MAY NOT
C****      BE VOLUMES AT EQUILB. SAMPLE TUBE MAY OR MAY NOT BE ISOLATED.
C**** NT,MT - VOLUMES AT EQUILB. WITH SAMPLE TUBE STOP COCK OPEN.
C**** PGL,PGR - HEIGHTS OF GAS THERMO. MANOMETER WHEN DATA POINT IS TAKEN.
C**** TR - ROOM TEMP. WHEN DATA POINT IS TAKEN.
C**** V2SYS - VOLUME OF SYSTEM WHEN VST IS BEING DETERMINED. ALL MEASUREMENTS
C****      ARE MADE WITH SAMPLE TUBE STOP COCK OPEN
C**** TVST - TEMP OF LIQ. N2 BATH IN WHICH SAMPLE TUBE IS EMERSED DURING
C****      SAMPLE TUBE VOLUME DETER.
C**** VSTAVG - AVERAGE VOLUME OF SAMPLE TUBE FROM MPOINT DATA POINTS.
```

```
C**** MPOINT - NO. OF DATA POINTS USED TO CALCULATE VSTAVG.  (GE.2 ,LE.12)
C**** ERROR - ERROR IN VST CALCULATIONS
C**** VSYSA - VOLUME OF SYSTEM WITH SAMPLE TUBE STOP COCKS CLOSED AFTER
C****     ORIGINAL AMT. OF ADSORBATE HAS BEEN ADDED BEFORE ADSORPTION AAS
C****     TAKEN PLACE
C**** VADS - VOLUME OF ORIGINAL ADSORBATE AT STP
C**** VSYSM - VOLUME OF SYSTEM WHEN PRESSURE READINGS PL,PR ARE TAKEN
C**** VSYS - VOLUME OF SYSTEM AT EQUILB. AFTER READINGS OF PL,PR
C**** PP - EQUILB. PRESSURE AFTER SAMPLE HAS ADSORBED AT EACH PRESS. INCREMENT.
C****     THIS PRESS. IS VALID FOR THE CASE IN WHICH THE SAMPLE TUBE STOP COCK
C****     IS OPEN. THEREFORE CALC. WITH THIS PRESS. MUST TAKE INTO ACCT. THE
C****     VOLUME OF THE SAMPLE TUBE.
C**** TN2 - TEMP. OF LIQ. N2 BATH AT EACH POINT.
C**** V - VOLUME OF ADSORBATE PRESENT AT EACH POINT.
C**** VADSI - VOLUME OF ADS. ADSORBED AT EACH POINT.
C**** VBAR - VOL ADS/GM SAMPLE AT EACH POINT
C**** PO - VAPOR PRESSURE OF ADS. AT EACH POINT
C**** X - REDUCED PRESSURE
C**** PAL21,PAR21,NA21,MA21,TRA21 - MEASUREMENTS WITH SAMPLE TUBE STOP COCK
C****     CLOSED AFTER MAX. REDUCED PRESSURE OBTAINABLE WITH ORIGINAL
C****     ADS. ADDED HAS BEEN REACHED
C**** PAL22,PAR22,MA22,NA22,TRA22 - MEASURMENTS WITH SAMPLE TUBE STOP COCK
C****     CLOSED AFTER ADDITIONAL ADS. HAS BEEN ADDED
C**** VADSAD - VOLUME OF ADD. ADS.
C**** SLOPE - SLOPE OF LEAST SQUARES LINE
C**** B - INTERCEPT OF LEAST SQUARES LINE
C**** YCALC(I) - CALCULATED Y(I) VALUES
C**** VBARC(I) - CALCULATED VALUES OF VBAR(I)
C**** ECORR - CORRELATION ERROR BETWEEN Y(I) AND YCALC(I)
C**** EVBAR - CORRELATION ERROR BETWEEN VBAR(I) AND VBARC(I)
C**** C -
C**** VBARM - VOLUME OF N2 NEEDED TO FORM MONOLAYER (CC/GM)
C**** XM - WEIGHT OF ADSORBATE
C**** SAREA - SPECIFIC SURFACE AREA (METER**2/GM)
      DIMENSION HEAD(26),ADSORB(5,3),GAS(5,3),VOL(10),PL(12),PR(12),
     *NT(12),MT(12),TR(12),PGL(12),PGR(12),PP(12),PG(12),VSYS(12)
      DIMENSION MON(12),IASB(4),IGAS(6),P2L(12),P2R(12),NV2(12),MV2(12),
     *V2SYS(12),P2VST(12),
     *TN2(12),V(12),VADSI(12),VBAR(12),PO(12),X(12),Y(12),W(12),
     *YCALC(12),VBARC(12),VST(12),NTM(12),MTM(12),VSYSM(12)
```

```
      DATA ((ADSORB(I,J),J=1,3),I=1,2)/28.02,16.2,.000066,83.8,18.5,0.0/
      DATA ((GAS(I,J),J=1,3),I=1,3)/6.866,308.365,273.20,7.177,525.695,
     . 273.16,7.5741,408.15,273.16/
      DATA VOL/66.225,31.841,26.652,11.130,2.567,70.006,41.363,17.702,
     .8.386,2.891/
      DATA VOLB/1.371/
      DATA VOLC/1.373/
      DATA MON/'JAN','FEB','MAR','APR','MAY','JUN','JUL','AUG','SEP',
     .'OCT','NOV','DEC'/
      DATA IASB/'NITROGEN    ','KRYPTON     '/,
     .      IGAS/'NITROGEN    ','KRYPTON     ','ARGON       '/
      REAL M
  100 FORMAT (13A6)
  101 FORMAT (10X,F10.0)
  102 FORMAT (10X,A2)
  103 FORMAT (10X,A3)
  104 FORMAT (5X,'.... INCORRECT ADSORBATE REQUESTED. CODE REQUESTED IS'
     .,5X,A2 )
  105 FORMAT (5X,'.... INCORRECT THERMOMETER GAS REQUESTED. CODE REQUEST
     .ED WAS ',5X,A2 )
  106 FORMAT (5X,'.... INCORRECT VOLUME VB OR VC REQUESTED. CODE REQUEST
     .ED ',5X,A2 )
  107 FORMAT (10X,2F10.0,2I10)
  108 FORMAT (10X,7F10.0)
  109 FORMAT (10X,2F10.0,2I10,F10.0)
  110 FORMAT (5X,'.... NUMBER OF DATA POINTS IS OUT OF RANGE. NO. OF POI
     .NTS = ',I5 )
  111 FORMAT (10X,2F10.0,4I10)
  112 FORMAT (5X,'..... THE NUMBER OF POINTS USED IN THE CALCULATION OF
     .THE VOLUME OF THE SAMPLE TUBE IS WRONG'/,5X,'NO. POINTS =',I5 )
  113 FORMAT (5X,  '.... TWO SUCCESSIVE PRESSURES ON TH SAMPLE TUBE ARE
     .EQUAL .....' )
  114 FORMAT (10X,3F10.0)
  141 FORMAT (A6)
  200 FORMAT ('1',1X,'PAGE ',I3,85X,I2,2X,A3,'  19',I2)
  201 FORMAT (//,26X,'DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E
     .T METHOD')
  202 FORMAT (/49X,'INPUT DATA')
  203 FORMAT (//,6X,'SAMPLE DESCRIPTION  ',13A6/,26X,13A6)
  204 FORMAT (//6X,'SAMPLE WEIGHT (GRAMS)  ',F10.4,6X,'ADSORBATE  ',
     .2A6,6X,'THERMOMETER GAS  ',2A6 )
 205 FORMAT (/47X,'SAMPLE HOLDER  ',A1 )
 206 FORMAT (//,15X,'VAPOR PRESSURE EQUATIONS',36X,'DETERMINATION OF')
 207 FORMAT (23X,'(MM HG)',41X,'STP VOLUME OF ADSORBATE')
 208 FORMAT (/,20X,'THERMOMETER GAS',25X,'INITIAL ADSORBATE PRESSURE',
     .7X,'NUMBERS FOR')
 209 FORMAT (60X,'MANOMETER READINGS (MM HG)',5X,'VOLUMES FILLED')
 210 FORMAT (7X,'LOG(10) P =',F7.3,' -',F6.2,' / (T +',F6.1,')')
 211 FORMAT (67X,'LEFT',6X,'RIGHT',13X,'N',4X,'M')
 212 FORMAT (64X, F7.2,4X,F7.2,12X,I2,3X,I2)
 213 FORMAT (23X,'ADSORBATE')
 214 FORMAT (/7X,'LOG(10) P =',F7.3,' -',F6.2,' / (T +',F6.1,')' ,
     .14X,'SYSTEM TEMPERATURE',F9.1,'  DEG. K' )
 215 FORMAT (//58X,'ORIGINAL VOLUME OF ADSORBATE AT STP =',F9.2,' CC')
 216 FORMAT (//40X,'SAMPLE TUBE VOLUME CALIBRATION')
 217 FORMAT (//20X,'HELIUM PRESSURE',22X,'NUMBERS FOR',16X,'VOLUME OF')
 218 FORMAT (15X,'MANOMETER READINGS (MM HG)',15X,'BULBS FILLED',15X,
     .'SYSTEM (ML)')
 219 FORMAT (/22X,'LEFT',6X,'RIGHT',23X,'N',4X,'M')
 220 FORMAT(19X,F7.2,F11.2,22X,I2,3X,I2,19X,F7.2)
 221 FORMAT (//12X,'SAMPLE TEMPERATURE DETERMINATION',23X,'SYSTEM TEMPE
     .RATURE DETERMINATION')
 222 FORMAT (/15X,'GAS THERMOMETER PRESSURE')
 223 FORMAT ( 15X,'MANOMETER READING (MM HG)',29X,'SYSTEM TEMPERATURE (
     .DEG. K)')
 224 FORMAT (/,21X,'LEFT',8X,'RIGHT',41X,F7.1)
 225 FORMAT (18X,F7.2,6X,F7.2)
 226 FORMAT (//39X,'SAMPLE TUBE VOLUME =',F9.2,' CC' )
 227 FORMAT (//,47X,'ADSORTION DATA')
 228 FORMAT (//,8X,'ADSORBATE PRESSURE',10X,'NUMBERS FOR',14X,'THERMOME
     .TER GAS',17X,'ROOM' )
 229 FORMAT (8X,'MANOMETER READINGS',8X,'VOLUMES FILLED',17X,'PRESSURE'
     .17X,'TEMPERATURE')
 230 FORMAT (13X,'(MM HG)',36X,'MANOMETER READINGS (MM HG)',8X,'(DEGREE
     .S K)' )
 231 FORMAT (/13X,'LEFT',4X,'RIGHT',13X,'N',5X,'M',18X,'LEFT',6X,
     .'RIGHT')
 232 FORMAT (6X,I2,F9.2,F9.2,12X,I2,4X,I2,15X,F7.2,4X,F7.2,14X,F7.1)
 233 FORMAT (26X,'DETERMINATION OF SPECIFIC SURFACE AREA BY THE B E T M
     .ETHOD')
```

```
      234 FORMAT (/,27X,'B E T EQUATION:    F/V(PO-P) = ((C-1)/VM•C)P/PO + 1
         •/VM•C' )
      235 FORMAT (//7X,'SAMPLE',11X,'REDUCED',8X,'VOLUME ADSORBED PER GRAM',
         •11X,'P/V(PO-P)',11X,'NORMALIZED')
      236 FORMAT (5X,'TEMPERATURE'5X,'PRESSURE P/PO',10X,'SAMPLE AT STP',
         •18X,'(G/ML)',14X,'WEIGHTING')
      237 FORMAT (6X,'(DEG. K)',10X,'(MM HG)',17X,'(ML/G)',41X,'FUNCTION')
      238 FORMAT (/40X,'OBSERVED',3X,'CALCULATED',7X,'OBSERVED',3X,'CALCULAT
         •ED')
      239 FORMAT (7X,F7.1,10X,F7.3,10X,F7.3,6X,F7.3,8X,F7.5,6X,F7.5,7X,F7.2)
      240 FORMAT(/18X,'VOLUME ABSORBED PER GRAM SAMPLE IN MOLECULAR MONOLAYE
         •R (VM) =',F8.2,'  ML/G')
      241 FORMAT(/20X,'RELATIVE LIFETIMES OF MOLECULES IN FIRST AND HIGHER L
         •AYERS (C) =',F8.2)
      242 FORMAT (/9X,'CORRELATION ERROR FOR P/V(PO-P) =',F8.5,9X,'C-1/VM•C
         •=',F8.4,9X,'1/VM•C =',F8.5)
      243 FORMAT (/ 14X,'RMS ERROR FOR VOLUME ADSORBED =',F8.2,16X,'ERROR IN
         • C-1/VM•C = ',F8.4)
      244 FORMAT (/21X,'ERROR IN 1/VM•C = ',F8.5,21X,'ERROR IN VM = ',F8.2)
      245 FORMAT (/37X,'SPECIFIC SURFACE AREA = 'F7.2,' • VM')
      246 FORMAT (/30X,'SPECIFIC SURFACE AREA ='F8.2,'  SQUARE METERS/GRAM'
         •)
      247 FORMAT (/35X,'ERROR IN SPECIFIC SURFACE AREA = ',F7.2)
      248 FORMAT (36X,'ERROR IN SAMPLE TUBE VOLUME =',F8.4)
          READ 100,HEAD
          READ 101,VOLA
          VOLT = 0.0
          DO 82 I=1,10
       82 VOLT = VOLT +VOL(I)
          VOLT = VOLT+VOLA
          READ 101,WS
          READ 102,NASB
          READ 102,NGAS
          READ 102,IV
          READ 103,IWEIGH
          IF (NASB.EQ.2HN2)GO TO 1
          IF (NASB.EQ.2HKR)GO TO 2
          PRINT 104,NASB
          STOP
C•••• NITROGEN ADSORBATE
```

```
    1 CONTINUE
      IAD1= IASB(1)
      IAD2= IASB(2)
      M = ADSORB(1,1)
      AM =ADSORB(1,2)
      ALPHA = ADSORB(1,3)
      AS = GAS(1,1)
      BS = GAS(1,2)
      CS = GAS(1,3)
      GO TO 3
C**** KRYPTON ADSORBATE
    2 CONTINUE
      AS = GAS(2,1)
      BS = GAS(2,2)
      CS = GAS(2,3)
      IAD1= IASB(3)
      IAD2= IASB(4)
      M = ADSORB(2,1)
      AM = ADSORB(2,2)
      ALPHA = ADSORB(2,3)
    3 CONTINUE
      IF (NGAS.EQ.2HN2)GO TO 5
      IF (NGAS.EQ.2HKR)GO TO 6
      IF (NGAS.EQ.2HAR)GO TO 7
      PRINT 105,NGAS
      STOP
C**** NITROGEN GAS
    5 CONTINUE
      IGS1= IGAS(1)
      IGS2= IGAS(2)
      AG = GAS(1,1)
      BG = GAS(1,2)
      CG = GAS(1,3)
      GO TO 8
C**** KRYPTON GAS
    6 CONTINUE
      IGS1= IGAS(3)
      IGS2= IGAS(4)
      AG = GAS(2,1)
      BG = GAS(2,2)
      CG = GAS(2,3)
      GO TO 8
C**** ARGON GAS
    7 CONTINUE
      IGS1= IGAS(5)
      IGS2= IGAS(6)
      AG = GAS(3,1)
      BG = GAS(3,2)
      CG = GAS(3,3)
    8 CONTINUE
      IF (IV.EQ.2HVB)GO TO 9
      IF (IV.EQ.2HVC)GO TO 10
      PRINT 106,IV
      STOP
C**** VOLUME VB USED
    9 CONTINUE
      IVBC =1HB
      VBC =VOLB
      GO TO 11
C**** VOLUME VC USED
   10 CONTINUE
      IVBC =1HC
      VBC = VOL C
   11 CONTINUE
C**** READ P,V,T MEASUREMENTS FOR VST CALCULATIONS
      MPOINT = 0
   43 READ 141,IEND
      IF (IEND.EQ.6HEND OF)GO TO 42
      MPOINT = MPOINT +1
      I=MPOINT
      READ (30,107)P2L(I),P2R(I),NV2(I),MV2(I)
      GO TO 43
   42 CONTINUE
      IF (MPOINT.GT.1.AND.MPOINT.LT.13)GO TO 34
      PRINT 112,MPOINT
      STOP
   34 CONTINUE
      READ 108,PGTL,PGTR,TRVST
      READ 109,PAL,PAR,NA,MA.TRA
      NPOINT = 0
   44 READ 141,IEND
      IF (IEND.EQ.6HEND OF)GO TO 45
      NPOINT = NPOINT +1
      I= NPOINT
      READ (30,111)PL(I),PR(I),NTM(I),MTM(I),NT(I),MT(I)
      READ 114,PGL(I),PGR(I),TR(I)
      GO TO 44
   45 CONTINUE
      IF (NPOINT.LE.12)GO TO 12
      PRINT 110,NPOINT
      STOP
   12 CONTINUE
C**** CALCULATIONS FOR SAMPLE TUBE
      DO 36 I=1,MPOINT
      P2VST(I)= P2L(I)-P2R(I)
      V2SYS(I)= 0.0
      SUM1= 0.0
      SUM2= 0.0
      IPN = NV2(I)
      IPM = MV2(I)
      IF (IPN.EQ.0)GO TO 18
      DO 19 J=1,IPN
   19 SUM1 = SUM1 + VOL(J)
   18 IF (IPM.EQ.0)GO TO 20
      DO 21 J=6,IPM
   21 SUM2 = SUM2 + VOL(J)
   20 CONTINUE
   36 V2SYS(I)= VOLT - SUM1 - SUM2
      PGTVST = PGTL- PGTR
      TVST = BG/(AG-ALOG10(PGTVST)) - CG
      TLVST = TVST + 273.16
      TSVST = TRVST + 273.16
      NM1 = MPOINT -1
      DO 48 I=1,NM1
      VST(I) = TLVST*(P2VST(I)*(V2SYS(I)+VBC)- P2VST(I+1)*(V2SYS(I+1)
     *   +VBC))/(TSVST*(P2VST(I+1)-P2VST(I)))
      PP2 = P2VST(I+1)- P2VST(I)
      IF (PP2.NE. 0.0)GO TO 48
      PRINT 113
      STOP
   48 CONTINUE
      VSTAVG = 0.0
      DO 49 I=1,NM1
   49 VSTAVG = VSTAVG + VST(I)
      VSTAVG =  VSTAVG /NM1
      TEMP = 0.0
      DO 50 I=1,NM1
   50 TEMP = TEMP + (VSTAVG- VST(I))**2
      ERROR = SQRT(TEMP/NM1)
C**** CALCULATIONS FOR ADSORBATE
      PA = PAL - PAR
      VSYSA = 0.0
      SUM1= 0.0
      SUM2= 0.0
      IF (NA.EQ.0)GO TO 22
      DO 23 I=1,NA
   23 SUM1= SUM1 + VOL(I)
   22 IF (MA.EQ.0)GO TO 24
      DO 25 I=6,MA
   25 SUM2 = SUM2 + VOL(I)
   24 CONTINUE
      VSYSA = VOLT - SUM1 - SUM2
      TSYSA = TRA + 273.16
      VADS =  VSYSA*PA/(TRA+273.16)*.3592105
C**** CALCULATIONS FOR EACH DATA POINT
      DO 26 I=1,NPOINT
      PP(I)= PL(I)-PR(I)
      PG(I)= PGL(I)-PGR(I)
      VSYS(I)= 0.0
      VSYSM(I) = 0.0
      SUM1 = 0.0
      SUM2 = 0.0
      IF (NT(I).EQ.0)GO TO 27
      IP= NT(I)
      DO 28 J=1,IP
   28 SUM1= SUM1 + VOL(J)
   27 IF (MT(I).EQ.0)GO TO 29
      IP = MT(I)
      DO 30 J=6,IP
   30 SUM2 = SUM2 + VOL(J)
   29 CONTINUE
      SUM1M=0.0
      SUM2M=0.0
      IF (NTM(I).EQ.0)GO TO 54
      IP = NTM(I)
      DO 55 J=1,IP
   55 SUM1M = SUM1M +VOL(J)
   54 IF (MTM(I).EQ.0)GO TO 56
      IP=MTM(I)
      DO 57 J=6,IP
   57 SUM2M=SUM2M+VOL(J)
   56 CONTINUE
      VSYSM(I) = VOLT - SUM1M-SUM2M
      VSYS(I) = VOLT - SUM1 - SUM2
      PP(I)= PP(I)*VSYSM(I)/VSYS(I)
      TN2(I) = 273.16-BG/(ALOG10(PG(I))-AG) - CG
      V(I) = (VSYS(I) + (VBC+.047))*PP(I) / (TR(I) + 273.16)*.3594736
     *   +(VSTAVG-.047)*(1.0+ALPHA*PP(I))*PP(I)/TN2(I)*.3594736
      VADSI(I) =  VADS - V(I)
      VBAR(I) = VADSI(I)/WS
      PO(I) =  10.0 **(AS - (BS/(TN2(I)-273.16 + CS)))
      X(I) = PP(I)/PO(I)
      Y(I) = PP(I)/(VBAR(I)*(PO(I)- PP(I)))
   26 CONTINUE
      NMAX = NPOINT
      READ 100,ISTOP
      IF (ISTOP.NE.6HADDITI)GO TO 58
      ISTOP = 1
      READ 109,PAL21,PAR21,NA21,MA21,TRA21
      READ 109,PAL22,PAR22,NA22,MA22,TRA22
   59 READ 141,IEND
      IF (IEND.EQ.6HEND OF)GO TO 60
      NPOINT = NPOINT + 1
      I = NPOINT
      IF (NPOINT.LE.12)GO TO 61
      PRINT 110,NPOINT
      STOP
   61 CONTINUE
      READ (30,111)PL(I),PR(I),NTM(I),MTM(I),NT(I),MT(I)
      READ 114,PGL(I),PGR(I),TR(I)
      GO TO 59
   58 ISTOP =0
   60 CONTINUE
      IF (ISTOP.EQ.0)GO TO 62
      PA21 = PAL21-PAR21
      VA21=0.0
      SUM1 = 0.0
      SUM2 = 0.0
      IF(NA21.EQ.0)GO TO 63
      DO 64 I=1,NA21
   64 SUM1 = SUM1 + VOL(I)
   63 IF(MA21.EQ.0)GO TO 65
      DO 66 I=6,MA21
   66 SUM2 = SUM2 + VOL(I)
   65 CONTINUE
      VA21   = VOLT- SUM1- SUM2
      TSYSA2 = TRA21+ 273.16
      VADS21 = VA21 * PA21/(TRA21+273.16)*.3592105
      PA22 = PAL22-PAR22
      VA22=0.0
      SUM1=0.0
      SUM2=0.0
      IF (NA22.EQ.0)GO TO 79
      DO 80 I=1,NA22
   80 SUM1=SUM1+VOL(I)
   79 IF (MA22.EQ.0)GO TO 81
      DO 83 I=6,MA22
   83 SUM2=SUM2+VOL(I)
   81 CONTINUE
      VA22 = VOLT-SUM1-SUM2
      VADS22=VA22*PA22/(TRA22+273.16)*.3592105
      VADSAD = VADS22-VADS21
      VADNEW = VADS+VADSAD
      NST = NMAX +1
      DO 67 I=NST,NPOINT
      PP (I) = PL(I)- PR(I)
      PG(I)= PGL(I)-PGR(I)
      VSYS(I) = 0.0
      VSYSM(I) = 0.0
      SUM1 = 0.0
      SUM2 = 0.0
      IF (NT(I).EQ.0)GO TO 68
      IP = NT(I)
      DO 69 J=1,IP
   69 SUM1 = SUM1 +VOL(J)
   68 IF (MT(I).EQ.0)GO TO 70
      IP = MT(I)
      DO 71 J=6,IP
   71 SUM2 = SUM2 + VOL(J)
   70 CONTINUE
      SUM1M = 0.0
      SUM2M = 0.0
      IF (NTM(I).EQ.0)GO TO 72
      IP = NTM(I)
      DO 73 J=1,IP
   73 SUM1M= SUM1M +VOL(J)
   72 IF (MTM(I).EQ.0)GO TO 74
      IP = MTM(I)
      DO 75 J=6,IP
   75 SUM2M= SUM2M + VOL(J)
   74 CONTINUE
      VSYSM(I) = VOLT - SUM1M-SUM2M
      VSYS(I) = VOLT -SUM1-SUM2
      PP(I)= PP(I)* VSYSM(I)/VSYS(I)
      TN2(I)= 273.16 - BG/(ALOG10(PG(I))-AG)-CG
      V(I) = (VSYS(I)+ (VBC+.047))*PP(I)/(TR(I)+273.16)*.3594736
     *  +(VSTAVG-.047)*(1.0 +ALPHA*PP(I))*PP(I)/TN2(I)*.3594736
      VADSI(I) = VADNEW-V(I)
      VBAR(I) = VADSI(I)/WS
      PO(I) = 10.0**(AS - (BS/(TN2(I)-273.16 + CS)))
      X(I)= PP(I)/PO(I)
      Y(I)= PP(I)/(VBAR(I)*(PO(I)-PP(I)))
   67 CONTINUE
   62 CONTINUE
      IF (NPOINT.GE.5)GO TO 76
      PRINT 110,NPOINT
      STOP
   76 CONTINUE
      IF (IWEIGH.EQ.6HNO    )GO TO 46
      GO TO 47
   46 DO 31 I=1,NPOINT
   31 W(I)= 1.0
   47 CONTINUE
      SW= 0.0
      SWYX = 0.0
      SWY = 0.0
      SWX = 0.0
      SWXX = 0.0
      DO 32 I=1,NPOINT
      SW = SW + W(I)
      SWYX = SWYX + W(I)*Y(I)*X(I)
      SWY = SWY + W(I)* Y(I)
      SWX = SWX + W(I)* X(I)
   32 SWXX= SWXX + W(I)*X(I)*X(I)
      SLOPE = (SW*SWYX - SWY*SWX)/(SW*SWXX-SWX*SWX)
      B= (SWYX*SWX-SWXX*SWY)/(SWX*SWX-SW*SWXX)
      SCOR =0.0
      SV=0.0
      DO 33 I=1,NPOINT
      YCALC(I) =  SLOPE * X(I) + B
      VBARC(I) = PP(I)/(PO(I)-PP(I))/YCALC(I)
      SCOR = SCOR+W(I)*(Y(I)-YCALC(I))**2
   33 SV =  SV + (VBAR(I)- VBARC(I))**2
      ECORR =  SQRT (SCOR/NPOINT)
      ERRINT = SQRT (SWXX/(NPOINT*SWXX-SWX*SWX))*ECORR
      ERRSLO = SQRT (NPOINT/(NPOINT*SWXX-SWX*SWX))*ECORR
      ERRVM = SQRT(ERRSLO**2 + ERRINT**2)/(SLOPE + B)**2
      EVBAR = SQRT(SV/NPOINT)
      C =  1.0 + SLOPE/B
      CONS = 6.02*AM/22.414
      ERRSSA = CONS*ERRVM
      VBARM = 1.0/(B+SLOPE)
      XM = VBARM * M/22414.0
      SAREA = XM* 6.02 * AM *1000.0/M
      CALL DATE (MONTH,IDAY,IYEAR)
      IMONTH = MON(MONTH)
      IPAGE = 1
      PRINT 200,IPAGE,IDAY,IMONTH,IYEAR
      PRINT 201
      PRINT 202
      PRINT 203,HEAD
      PRINT 204,WS,IAD1,IAD2,IGS1,IGS2
      PRINT 205IVBC
      IF (ISTOP.EQ.1)GO TO 77
      PRINT 206
      PRINT 207
      PRINT 208
      PRINT 209
      PRINT 210,AG,BG,CG
      PRINT 211
      PRINT 212,PAL,PAR,NA,MA
      PRINT 213
      PRINT 214,AS,BS,CS,TSYSA
      PRINT 215,VADS
      GO TO 78
   77 CONTINUE
      PRINT 249
  249 FORMAT (//14X,'DETERMINATION OF STP VOLUME',28X,'DETERMINATION OF
     .STP VOLUME')
      PRINT 250
  250 FORMAT (14X,'OF ORIGINAL ADSORBATE ADDED',27X,'OF ADDITIONAL ADSOR
     .BATE ADDED')
      PRINT 251
  251 FORMAT(/5X,'INITIAL ADSORBATE PRESSURE',7X,'NUMBERS FOR',10X,'INIT
     .IAL ADSORBATE PRESSURE',7X,'NUMBERS FOR' )
      PRINT 252
  252 FORMAT (5X,'MANOMETER READINGS (MM HG)',5X,'VOLUMES FILLED',10X,
     .'MANOMETER READINGS (MM HG)',5X,'VOLUMES FILLED')
      PRINT 253
  253 FORMAT(/12X,'LEFT',6X,'RIGHT',13X,'N',4X,'M',21X,'LEFT',6X,'RIGHT'
     .,13X,'N',4X,'M' )
      PRINT 254,PAL,PAR,NA,MA,PAL21,PAR21,NA21,MA21,PAL22,PAR22,NA22,
     .MA22
  254 FORMAT (9X,F7.2,4X,F7.2,12X,I2,3X,I2,  18X,F7.2,4X,F7.2,12X,I2,3X,
     .I2/  ,64X,F7.2,4X,F7.2,12X,I2,3X,I2//)
      PRINT 255,TRA,TRA21
  255 FORMAT (10X,'SYSTEM TEMPERATURE',F9.1,'  DEG. K',20X,'SYSTEM TEMPE
     .ATURE',F9.1,'  DEG. K' )
      PRINT 256,VADS,VADNEW
  256 FORMAT (/3X,'ORIGINAL VOLUME OF ASORBATE AT STP =',F9.2,' CC',
     • 5X,'ADDITIONAL VOLUME OF ADSORBATE AT STP =',F9.2,' CC')
      PRINT 257
  257 FORMAT (//,43X,'VAPOR PRESSURE EQUATIONS'/,51X,'(MM HG)'//,
     •48X,'THEMOMETER GAS' )
      PRINT 258,AG,BG,CG
  258 FORMAT ( 35X,'LOG(10) P =',F7.3,' -',F6.2,' / (T +',F6.1,')')
      PRINT 259
  259 FORMAT (//,50X,'ADSORBATE' )
      PRINT 258,AS,BS,CS
   78 CONTINUE
      IPAGE=2
      PRINT 200,IPAGE,IDAY,IMONTH,IYEAR
      PRINT 201
      PRINT 202
      PRINT 203,HEAD
      PRINT 216
      PRINT 217
      PRINT 218
      PRINT 219
      DO 51 I=1,MPOINT
      NNN= NV2(I)
      MMM= MV2(I)
   51 PRINT 220,P2L(I),P2R(I),NNN,MMM,V2SYS(I)
      PRINT 221
      PRINT 222
      PRINT 223
      PRINT 224,TSVST
      PRINT 225,PGTL,PGTR
      PRINT 226,VSTAVG
      PRINT 248,ERROR
      IPAGE = 3
      PRINT 200,IPAGE,IDAY,IMONTH,IYEAR
      PRINT 201
      PRINT 202
      PRINT 203,HEAD
      PRINT 227
      PRINT 228
      PRINT 229
      PRINT 230
      PRINT 231
      DO 52 I=1,NPOINT
      TT=273.16+TR(I)
   52 PRINT 232,I,PL(I),PR(I),NT(I),MT(I),PGL(I),PGR(I),TT
      IPAGE = 4
      PRINT 200,IPAGE,IDAY,IMONTH,IYEAR
      PRINT 233
      PRINT 203,HEAD
      PRINT 234
      PRINT 235
      PRINT 236
      PRINT 237
      PRINT 238
      DO 53 I=1,NPOINT
   53 PRINT 239,TN2(I),X(I),VBAR(I),VBARC(I),Y(I),YCALC(I),W(I)
      PRINT 240,VBARM
      PRINT 241,C
      PRINT 242,ECORR,SLOPE,B
      PRINT 243,EVBAR,ERRSLO
      PRINT 244,ERRINT,ERRVM
      PRINT 245,CONS
      PRINT 246,SAREA
      PRINT 247,ERRSSA
      END

    0 DIAGNOSTIC MESSAGES.
```

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

30 April 1969

T. Parsons
D. DeBerry
G. Schroeder

BI-MONTHLY PROGRESS REPORT NO. 8

EXPERIMENTAL STUDIES AND ECONOMIC FEASIBILITY STUDIES PROGRESS REPORT

I. INTRODUCTION

The objectives of this report are to present the data that have been collected up to this point in the experimental program for the dry metal oxides sorption study, and to describe the studies which predict the economic feasibility of the SO_2 sorption process for each dry metal oxide. A complete discussion of the kinetic studies has been given. This report serves mainly to describe the progress and success of the program to date.

II. EXPERIMENTAL STUDIES

As a result of the thermodynamic screening process described previously there has been compiled a list of metals whose oxides have been found to be thermodynamically capable of sorbing SO_2 under specified conditions. The economic feasibility of using these oxides as sorbents cannot be determined, however, without some knowledge of the rate of their reaction with SO_2 in a flue gas atmosphere. The experimental program designed for determining these necessary kinetic data consists of the following parts:

A. Compound Preparation

The selected oxides had to be prepared in a kinetically active form. Pure oxides purchased commercially are often prepared using methods that cause them to be inactive. One such method involves heating to high temperatures and results in sintering and reduction in surface area. The oxides had to be prepared with large surface areas and amorphous, rather than highly crystalline, structure. In general, the oxides were prepared by precipitating the hydroxide and drying and calcining it at the lowest possible temperature at which most of the water could be removed. Compounds which appeared inactive and of low surface area were prepared again using a different method (see Table I, nickel oxide 634-41-1, 634-65-2).

B. Compound Identification and Analysis

The metal oxides are being characterized by emission spectroscopy and atomic absorption spectroscopy by the Southwest Spectroscopic Laboratories, Dallas, Texas, to determine percent metal constituent and impurities present. The results have not yet been received.

The oxides have been analyzed using differential thermal analysis (DTA) to determine whether most of the water present has been

TABLE I: EXPERIMENTAL RESULTS

Compound	Preparation Method	X-ray Diffraction Pattern	BET Surface Area m^2g^{-1}	Kinetic Data for SO_2 Sorption									SO_2 Sorption Products from X-ray Diffraction
				n	$\frac{w_0}{m_0}$	T(°C)	k'^a	m	$P_{SO_2}{}^b$	k^c	E^d	A^e	
Copper Oxide 634-47-1	The oxide was prepared by precipitation of the hydroxide from the sulfate. The hydroxide was heated in the vacuum oven at 55°C for 44.5 hours.	The pattern agreed with that of CuO. The peaks were broad, indicating small crystal size or amorphous character.	52.04	3/2	1.01	352	0.0139	1	0.299	4.65	16.4	2.61	$CuSO_4$
						404	0.0310		0.306	10.1			$CuSO_4 \cdot 3H_2O$
						482	0.142		0.314	45.2			CuO
						404	0.0136		0.122	11.1			
				1/3	1.01	352	0.00642	1	0.299	2.15	20.3	29.7	
						404	0.0285		0.306	9.31			
						482	0.111		0.314	35.4			
						404	0.0112		0.122	9.18			
Cobalt Oxide 634-43-1	The oxide was prepared by calcination of the nitrate for 3 hours at 350°C and 3 hours at 100°C in vacuo.	The pattern agreed well with that for Co_3O_4. The peaks were sharp and well defined.	12.05	1	0.380	453	0.0200	1	0.318	6.29	19.4	4.36	β-$CoSO_4$
						544	0.0916		0.326	28.1			Co_3O_4
						453	0.00864		0.129	6.70			
Chromium Oxide 634-59-2	The oxide was prepared by calcination of $(NH_4)_2CrO_4$ at 180°C for 15 minutes.	The pattern agreed well with that of Cr_2O_3. The product was almost amorphous as indicated by the broad peaks.	66.52	DCE	0.106	335	0.00257	1	0.319	0.806			Diffraction pattern obtained with diffractometer inconclusive. The product appears to be amorphous.
						390	0.00481		0.312	1.54			
						336	0.00105		0.122	0.861			

The units are: a. min^{-1} b. atm $\times 10^2$ c. min^{-1} atm^{-m} d. kcal/mole e. min^{-1} atm^{-m} $\times 10^{-6}$

TABLE I: EXPERIMENTAL RESULTS (CONTINUED)

Compound	Preparation Method	X-ray Diffraction Pattern	BET Surface Area m^2g^{-1}	Kinetic Data for SO_2 Sorption									SO_2 Sorption Products from X-ray Diffraction
				n	$\frac{w_o}{m_o}$	T(°C)	k'^a	m	$P_{SO_2}{}^b$	k^c	E^d	A^e	
Tin Oxide 634-55-1	The hydroxide was precipitated from $SnCl_4$ and heated in the vacuum oven for 31 hours at 60°C. The oxide was calcined at 150°C for 3 hours.	No diffraction pattern was obtained using the diffractometer.	4.04										
Zinc Oxide 634-51-1	Zinc hydroxide was precipitated from the sulfate and heated in the vacuum oven for 23 hours at 60°C. The oxide was calcined for 1.5 hr. at 145°C and 1 hour at 100°C.	Diffraction pattern agreed well with that for ZnO. Peaks were sharp and well defined.	16.46										
Nickel Oxide 634-41-1	The oxide was prepared by calcining the nitrate for 1 hour at 300°C and 45 minutes at 380°C.	Diffraction pattern agreed well with that for NiO. Peaks were sharp and well defined.	7.02										
Nickel Oxide 634-65-2	The oxide was prepared by precipitating the hydroxide from the nitrate. The hydroxide was heated for	The diffraction pattern agreed well with that of NiO. The peaks were broad.	63.44	1/2	1.07	380	0.00764	1	0.322	0.232	13.5	.00781	$NiSO_4$
						500	0.00391		0.333	1.17			NiO
						501	0.00157		0.124	1.27			

The units are: a. min^{-1} b. atm $\times 10^2$ c. min^{-1} atm^{-m} d. kcal/mole e. min^{-1} atm^{-m} x 10^{-8}

TABLE L: EXPERIMENTAL RESULTS (CONTINUED)

Compound	Preparation Method	X-ray Diffraction Pattern	BET Surface Area m^2g^{-1}	Kinetic Data for SO_2 Sorption									SO_2 Sorption Products from X-ray Diffraction
				n	$\frac{w_0}{m_0}$	T(°C)	k'^{a}	m	$P_{SO_2}{}^{b}$	k^{c}	E^{d}	A^{e}	
Nickel Oxide 634-65-2 (Cont.)	18 hours at 70°C in vacuo, then heated in air at 330°C for 2 hours.												
Iron Oxide 634-45-1	The oxide was prepared by precipitation of the hydroxide from the chloride. The hydroxide was heated at 55°C in vacuo for 39 hours, at 120°C in vacuo for 1.5 hours and at 170°C in vacuo for 2 hours.	The pattern had very broad, uneasily distinguished peaks. Probably Fe_2O_3.	225.56	1/3	0.833	400	0.0108	1	0.306	3.53			Pattern obtained with diffractometer inconclusive. Peaks broad and not well defined.
						449	0.0109		0.309	3.53			
						400	0.00368		0.120	3.07			
Aluminum Oxide 634-53-1	The oxide was prepared by precipitation of the hydroxide from the chloride. Product was dried in vacuo for 50 hours at 60°C. The oxide was calcined for 3 hours at 280°C.	The pattern obtained with the diffractometer had no peaks.	322.54										
Zirconium Oxide 634-63-1	The oxide was prepared by precipitating the hydroxide from the sulfate.	The pattern obtained with the diffractometer had no peaks.	4.45										

The units are: a. min^{-1} b. atm $x10^{8}$ c. min^{-1} atm^{-m} d. kcal/mole e. min^{-1} atm^{-m} $x10^{-3}$

TABLE I: EXPERIMENTAL RESULTS (CONTINUED)

Compound	Preparation Method	X-ray Diffraction Pattern	BET Surface Area m^2g^{-1}	Kinetic Data for SO_2 Sorption									SO_2 Sorption Products from X-ray Diffraction
				n	$\frac{w_o}{m_o}$	T(°C)	k'^a	m	$P_{SO_2}{}^b$	k^c	E^d	A^e	
Zirconium Oxide 634-63-1 (Cont.)	The hydroxide was dried in the vacuum oven at 60°C for 24 hours and the oxide was calcined at 400°C for 2 hours.												
Antimony Oxide 634-67-1	The hydroxide was precipated from the pentachloride, dried at 70°C for 15 hours and calcined at 275°C for 2 hours.	The pattern agreed well with that of Sb_2O_5. The peaks were broad and not well defined.	18.28										
Cerium Oxide 634-37-1	The hydroxide was precipitated from ammonium hexanitrate cerate $[(NH_4)_2Ce(NO_3)_6]$ and dried in vacuo at 60°C.	The diffraction pattern was quite broad and the peaks almost undefined. It agreed with that of CeO_2.	192.66	2	0.251	191	0.0608		0.324				No peaks obtained with diffractometer. Better results could possibly be obtained from Debeye-Scherrer pattern.
						262	0.0504		0.320				
						194	0.0122		0.127				

The units are: a. min^{-1} b. atm. $x10^2$ c. min^{-1} atm^{-m} d. kcal/mole e. min^{-1} atm^{-m} $x10^{-8}$

removed during calcination. The samples were analyzed using the TRACOR LB-202 Recorder-Controller and JP-202 furnace platform. The results are given in the form of system temperature versus difference in temperature of a standard (Al_2O_3) and temperature of the sample. An endotherm results from hydroxide decomposition or loss of water of hydration. Although an endotherm also appears when a phase transition occurs, the cause of the peak is easily determined from its shape. A sharp peak is caused by melting, while decomposition results in a broader, more gradual change.

The oxides were identified from their x-ray powder diffraction patterns. The patterns were determined using Cr $K\alpha$ radiation with either a Siemens type F Diffractometer (technical description Eg 4/22e) or a Siemens short cylindrical camera for Debye-Scherrer patterns (cat. no. 176311). From the diffraction patterns it was possible not only to identify the phases present, but also, when the diffractometer was employed, to obtain an indication of the particle size and crystalline form. The lattice spacings were calculated from the diffraction angles according to the Bragg equation. Observed values were compared with those listed in the ASTM Inorganic Index to the Powder Diffraction File 1967.

C. Surface Area

As stated earlier, the magnitude of the surface area of a sample can have an effect on its activity. In the case of SO_2 sorption, a low surface area decreases the activity of a sample as compared to one with a higher surface area. Low surface area and poor kinetic data might indicate an oxide could be prepared again in a more active form.

The surface areas of the selected oxides were determined by the BET method (the method of Brunauer, Emmett, and Teller) which involves measuring the amount of gas adsorbed on the surface of a solid. The method is well known and widely applied. A detailed description of the apparatus used and calculations done at TRACOR will be described in a later report.

D. Kinetic Measurements

The measurement of the reaction rate of the thermodynamically favorable dry metal oxides with SO_2 is an important part of the overall screening process. Even the most thermodynamically capable sorbent may be of no use for SO_2 removal if it reacts too slowly to be economically feasible. The first step in these measurements was the determination of the temperature range in which the rate of SO_2 sorption was measurable. Isothermal rate measurements were then made at constant SO_2 partial pressure for several temperatures in this range. The temperature dependence of the reaction rate was calculated from these data. An isothermal run at a different SO_2 partial pressure then supplied the data for calculating the dependence of the reaction rate on partial pressure of SO_2.

All of these kinetic measurements were made by continuous recording of the weight gain of the sample as a function of time at constant temperature as SO_2 was admitted and sorbed by the sample. The weight gain data were then converted to extent of reaction data by using the initial weight of reactant and the total weight gain at long reaction times, or the stoichiometric weight gain if known.

1. Apparatus

A TRACOR TGA-3C thermal balance was used to make the kinetic measurements. In this instrument the sample holder is suspended from a spring. A photocell assembly in conjunction with a servo motor and linear actuator are used to maintain a null condition while displacing the core of a linear variable differential transformer (LVDT). This displacement results in a signal which is displayed as the weight change.

The most important and unique feature of the TGA-3C for this type of rate measurement is that the reactive gas is forced past the reactive solid. The gas enters the hollow connecting rod between the spring and sample holder and passes through the sample holder exiting from a porous frit or fine stainless steel screen at the bottom. Thus the gas composition actually surrounding the solid is known and one does not have to depend on molecular diffusion through particle interstices to supply the reactant to the solid.

The temperature was measured with a Pt-Pt/10% Rh thermocouple placed about 1 mm from the sample holder. The cylindrical Inconel sample holder is 1.3 cm in diameter and 2.8 cm long.

A TRACOR LB-202 Recorder-Controller was used with the TGA-3C to control and record the temperature and to amplify and record the weight change signal. The weight gain vs system temperature was recorded on a Moseley X-Y recorder. The 0°C reference point was set electronically. A Hewlitt-Packard model 17504 A strip chart recorder provided the isothermal weight gain vs time record.

The gas mixing and control apparatus has been described in T.M. 004-009-Ch20. This apparatus is capable of producing a wide range of gas compositions. Flows and pressures are reproducible and can be accurately controlled. Step changes in gas composition can be obtained without affecting the flow through the thermal balance system. Gas analysis equipment is included to provide an independent means of determining compositions and can be used without disturbing the flow to the experimental equipment.

2. Experimental Procedure

The particle size of all of the samples studied was 170-325 mesh (44-88 microns). Typically 10-50 mg of sample was mixed well with 1.0-1.1 g alumina in the sample holder. The weight of sample and alumina were determined by difference using a Mettler Type B6 analytical balance.

The temperature range of interest was determined by making a linear temperature programmed run using a simulated flue gas atmosphere. The sample was heated at 10°C/min in an atmosphere composed of the following:

Component	Mole Per Cent
SO_2	0.3
CO_2	14.3
O_2	3.4
H_2O	2.0
N_2	balance

This experiment indicated at what temperature the reaction of the metal oxide with SO_2 "started" or became fast enough to give a measurable weight gain and at what temperature the product began to decompose.

Two or more isothermal runs were then made at temperatures within this range. The thermal balance was mass calibrated before each run. The sample was heated in a nitrogen atmosphere at 20°C/min until the chosen temperature was reached. The temperature was then held constant by the Recorder-Controller. After thermal equilibrium was established, H_2O, CO_2, and O_2 were admitted to the gas stream. When this atmosphere was established and a straight baseline (zero weight change) was obtained on the strip chart recorder, SO_2 flow was started. The atmosphere thus obtained was the same as that given above. This procedure ensures that the weight gain measured will be due to sulfite or sulfate formation rather than carbonate or hydroxide formation or oxidation of the metal oxide.

Zero time for the reaction was taken as the point at which the weight gain began. The run was continued until there was little or no further weight gain. The temperature range of the reaction was recorded on the X-Y recorder as a horizontal of the weight change vs temperature graph. In most cases there was no more than ± 1°C variation in temperature. The SO_2 concentration of the stream was determined during each run by titration of a known amount of iodine (Reich's test).

The procedure used for the determination of the rate dependence on the partial pressure of SO_2 was the same as above except that the SO_2 concentration was set at 0.12 mole %.

The average total flow to the sample was 250 cc/min (linear velocity 6.2 ft/min). The sample size was kept small enough that the reaction rate did not become limited by the rate of SO_2 supply.

3. Data Analysis

The data obtained from these kinetic measurements were in the form of weight gain, w, as a function of time. The extent of reaction can be better represented as the fractional conversion $\alpha \equiv w/w_0$. Ideally w_0 is the theoretical stoichiometric weight gain. In practice it was found that often the stoichiometry of the reaction was not well defined or that the reaction rate became very slow before the stoichiometric weight gain was reached. In these cases w_0 was taken as the maximum weight gain recorded for a given compound, taking into account the initial weight of sorbent, m_0. The high temperature run was usually used to determine w_0. The calculations for the other runs for each compound were then based on the ratio w_0/m_0 which is given in Table I.

The rate of product formation can be defined as $\frac{d\alpha}{dt}$. In isothermal conditions it can be assumed that the reaction rate depends only upon the fraction reacted and the partial pressure of SO_2. This is expressed in Equation 1.

$$\frac{d\alpha}{dt} = k\ f(\alpha)\ g(P_{so_2}) \qquad (1)$$

where k is the rate constant. At Constant P_{so_2} Equation 1 can be written as

$$\frac{d\alpha}{dt} = k'\ f(\alpha) \qquad (2)$$

The analytical form of $f(\alpha)$ depends upon the mechanism of the reaction. For our present purposes the general form

$$f(\alpha) = (1-\alpha)^n \qquad (3)$$

and the form derived by assuming that the rate is controlled by diffusion to the unreacted core (DCE)

$$f(\alpha) = \frac{(1-\alpha)^{1/3}}{1 - (1-\alpha)^{1/3}} \qquad (4)$$

have been used. The constant n in Equation 3 has been assumed to be either 0, 1/3, 1/2, 2/3, 1, 3/2, or 2.

To determine the proper form of $f(\alpha)$, a plot of the integrated form of $f(\alpha)$ versus time was obtained for each $f(\alpha)$.

$$I(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \qquad (5)$$

The plot corresponding to the proper form of $f(\alpha)$ should yield a straight line with slope k'. The integrated forms for each $f(\alpha)$ are given in Appendix A. The Univac 1108 computer was used to calculate the values of each $I(\alpha)$ and to plot $I(\alpha)$ vs t for each equation. The equation which gave the best straight line was determined by inspection. The slope k' of the least squared regression line was computer calculated and the data and line were plotted by the CalComp plotter. Examples are given in Appendix B.

The SO_2 partial pressure dependence of the reaction rate was obtained by calculating k' for two runs at the same temperature but different P_{SO_2} and assuming that $g(P_{SO_2}) = P^m_{SO_2}$.

Rewriting Equation 1 gives 6a and 6b:

$$\frac{d\alpha}{dt} = k' f(\alpha) = k f(\alpha) P^m_{SO_2} \quad (6a)$$

$$m = \frac{\log k'_1/k'_2}{\log P_{1_{SO_2}} / P_{2_{SO_2}}} \quad (6b)$$

Once m was known, k was easily calculated from

$$k = \frac{k'}{P^m_{SO_2}} \quad (7)$$

In these experiments P_{SO_2} (in atm) is numerically equal to the measured concentration of SO_2 (assuming ideal gas behavior) since the sample holder is at atmospheric pressure.

4. Results

The experimental results obtained to date are summarized in Table I. Most of the column headings are explained in the Data Analysis section above. Preliminary comments on these results and the linking of kinetic and economic data are given below.

The rate equation which gives the best "fit" appears to depend on the metal oxide to which it is applied and sometimes on the extent of reaction. This suggests that the reaction mechanism or rate controlling step may be different for different metal oxides or at different stages of the reaction. For CuO, results are given based both on n = 3/2, which gives the best overall fit, and on $n = 1/3$, which gives the best fit in the "low" conversion range ($\alpha \leq 0.43$). Plots depicting the original data ($n = 0$) as well as those used to calculate rate constants are given in Appendix B.

With the exception of CeO_2, the reaction rates of all the oxides studied to date depend linearly ($m = 1$) on SO_2 partial pressure. The actual calculated values of m vary from 0.9 - 1.1. The experiments with CeO_2 are being repeated in order to resolve the discrepancy.

The temperature dependence of the reaction rate has been calculated for several compounds using the Arrhenius equation

$$k = Ae^{-E/RT} \tag{8}$$

where E is the activation energy and A is the pre-exponential or frequency factor. Due to our incomplete knowledge of the reaction mechanisms, the use of this equation must be interpreted for the present simply as an empirical means of describing the temperature dependence. If the rate controlling step is pore diffusion or bulk diffusion of the gas into the solid, the rate should vary as $T^{\frac{1}{2}}$ to $T^{\frac{3}{2}}$ respectively. The actual value of the exponent will probably depend on which diffusion mechanism predominates. Such behavior may explain the relative constancy of reaction rate with changes in temperature observed for Fe_2O_3 and perhaps CeO_2. More data must be obtained before conclusions can be drawn.

The data obtained from kinetic studies must be used to describe the reaction rate in economic calculations. For economic calculations the rate of reaction is described in terms of the rate of SO_2 removal. In particular, the rate is assumed to be linearly proportional to the concentration of SO_2 in the flue gas at any time. This relation is expressed

$$-\frac{1}{V_s}\frac{dN_{SO_2}}{dt} = K_R C_{SO_2} \qquad (9)$$

where V_s is the volume of sorbent, N_{SO_2} is the number of moles of SO_2 removed, C is the concentration of SO_2 in the flue gas, and K_R is in $\frac{\text{cm}^3 \text{ gas}}{\text{cm}^3 \text{ solid-sec}}$. The relation given in Equation 10 was used to convert rate constants obtained from kinetic measurements to the form necessary for use in the economic calculations describing the fluidized bed sorber.

$$K_R = \frac{k\, f(\alpha)\, \rho_s\, w_0\, RT}{60\, M\, m_0} \qquad (10)$$

In Equation 10 k, m_0, w_0 and $f(\alpha)$ have been described previously, ρ_s is the density of the sorbent, M is the molecular weight of SO_2, R is the gas constant in cm³ atm mole^{-1} $^\circ\text{K}^{-1}$, and T is the temperature in degrees Kelvin.

Note that since $f(\alpha)$ appears in Equation 10, a value of α must be specified before K_R can be calculated. The value of α used will be determined by economic considerations.

E. Discussion

The progress of the experimental program and the quality of the data obtained to date are encouraging. It is expected that recent improvements in x-ray techniques will enable us to identify more completely the reaction products and therefore describe the reaction mechanisms.

As has been previously stated Table I is simply a summary of some of the results obtained so far. There are two reasons for the lack of data for some compounds. Either the data have been measured and the results are incomplete and not yet calculated, or the data have been taken and the results show the kinetics might be improved by preparing the compound in a more active form. For example, nickel oxide was prepared in two different ways. The first preparation, from decomposition of the nitrate, reacted very slowly with SO_2. The NiO prepared by hydroxide decomposition had a higher surface area and broader x-ray diffraction peaks. This sample reacted with SO_2 at a significant rate. Thus the surface area and qualitative estimate of crystallinity provide a good guide to the reactivity of different preparations of the same metal oxide.

Although the Al_2O_3 sample had a high surface area and was nearly amorphous according to the x-ray diffraction pattern, it was nevertheless a poor SO_2 sorbent (low reactivity).

These results show that high surface area and amorphous character do not guarantee reactivity. If a compound has high surface area and amorphous character and is unreactive, it is probable that the kinetics cannot be improved. If a compound has low surface area and crystalline character as indicated by x-ray diffraction, it might be possible to improve the kinetics by a different preparation method.

III. ECONOMIC FEASIBILITY STUDIES

The dry metal oxide sulfur oxide removal process is composed of three steps: 1) sorption, 2) regeneration, and 3) sulfur recovery. A fluidized bed contactor (refer to T.M. 004-009-Ch19 for design information) was used for cost estimation of the sorber and regenerator. Cost information for the sulfur recovery step is to be supplied by HEW.

In making economic studies of the sulfur removal process it is necessary to estimate the gross annual operating cost and the total capital investment.

A. Total Capital Investment Cost

The basis of computing the capital investment cost is the purchase price of the major pieces of equipment (see TM 004-009-Ch11). To the purchase price is added amounts of money to account for the erection cost, piping cost, instrument cost, etc. These items are added as a percent of purchase price. Several investigators (LA-004, HA-002, AR-001) have shown how percentages of the purchase price may be applied to cover the cost of erection, instrumentation, etc. The percentage factors given by Lang (LA-004) were used in this study. These factors are given in Table II.

The purchase cost of a fluidized bed sorber depends on the basic reaction kinetics and particle size. Given a value for reaction kinetics and particle size, one can calculate the associated vessel size. The purchase cost of the fluidized bed contactor, along with the associated cyclone and draft fan was estimated (see TM-004-009-Ch14,Ch15A).

B. Gross Annual Operating Cost

The gross operating cost consists of direct, indirect, and fixed costs (see TM 004-009-Ch11). These costs include items

TABLE II

INSTALLATION COST FACTORS

NO.	ITEM	LANG FACTOR
1.	Purchased Equipment	1.00
2.	Erection Labor	.25
3.	Foundations and Platforms	.18
4.	Piping	.76
5.	Instruments	.15
6.	Insulation	.08
7.	Electrical	.10
8.	Buildings	.25
9.	Land and Yard Improvements	.13
10.	Utilities	.40
11.	Engineering and Construction	.66
12.	Contractor's Fee	.19
13.	Contingency	.59
14.	Working Capital	10% Fixed Capital

such as chemicals, labor, plant overhead, utilities, depreciation and insurance. The gross total yearly operating cost for a given process is the sum of all direct, indirect, and fixed charges (AR-001). These costs are further defined in Table III.

The sorption unit consists of three major pieces of equipment: (1) sorber, (2) cyclone, and (3) draft fan. The total capital investment and gross annual operating cost were calculated for a process utilizing copper oxide (CuO) as the dry metal oxide sorbent. The sorption temperature was 350°C (662°F) and the reaction rate constant was 135 $\frac{\text{cm}^3 \text{ gas}}{\text{cm}^3 \text{ solid-sec}}$ as determined by TGA measurements. The total capital investment was $6,849,000 and the gross annual operating cost was $1,058,000. These calculations are based on a 1400 MW power plant handling 2.5 million SCFM of flue gas with an inlet SO_2 concentration of 3000 PPM and an outlet concentration of 150 PPM. The total capital investment cost can be reduced by operating the sorber in parallel flow. Thus, by stacking five fluidized beds each handling 1/5 of the total flow, the total capital investment required would be $6,400,000 thus saving over $400,000. Another advantage that could be obtained by stacking the fluidized beds would be one of conserving considerable space, since the sorber vessel diameter would be reduced from 147 feet to 66 feet. This becomes of considerable interest when the sorber must be tied into an existing plant.

The above calculation procedures were computerized by TRACOR and examples of the computer printout sheets are given in Table IV.

The proper conversion of sorbent (value of α') utilized to give reasonable costs is part of the regenerator problem. Rough calculations on a thermal regeneration process have been started along with a complete overall heat and material balance. The sorbent circulation rate is calculated from a material balance around the sorber. Results of these calculations will be given in a later report.

TABLE III

COMPONENTS OF GROSS ANNUAL OPERATING COST

DIRECT COSTS	INDIRECT COSTS	FIXED COSTS
Raw Matl's and Chemicals	Payroll Burden	Depreciation
Direct Labor	Plant Overhead	Taxes
Supervision	Packaging & Shipping	Insurance
Maintenance	Waste Disposal	
Plant Supplies		
Utilities		

TABLE IV

SUMMARY OF ECONOMIC STUDIES
COMPUTER OUTPUT

```
PAGE   1                                                                                      28 APR 19

                                            INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                      2500000.000          DENSITY OF SOLID (LBS/FT**3)              100.000
PARTICLE DIAMETER (INCHES)                  .0450          INLET CONCENT. (MOLE PERCENT)              .00300
REACTION RATE (1/SEC)                   135.00000          OUTLET CONCENT. (MOLE PERCENT)             .00015
RATIO- SUPERFICIAL TO MIN. VEL.             4.000          VOL. WAKE / VOL. BUBBLE                      .320
TEMPERATURE (DEG. F.)                     666.000          FRACTION OF SOLIDS IN BUBBLE                 .000
INLET PRESSURE (PSIA)                      14.700


                                            OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                      5409880.700          INITIAL BUBBLE DIAMETER (FEET)               .194
DIAMETER OF BED (FEET)                    145.940          FINAL BUBBLE DIAMETER (FEET)                 .328
HEIGHT OF BED (FEET)                        1.214          INITIAL BUBBLE VEL. (FT/SEC)                5.763
HEIGHT OF VESSEL (FEET)                    73.470          FINIAL BUBBLE VEL. (FT/SEC)                 6.298
THICKNESS OF SHELL (INCHES)                  .454          MIN. MASS FLUX (LBS/HR-FT**2)             173.838
BED PRESSURE DROP (IN. WATER)                .277          MIN. FLUID VOIDAGE                           .450
DISTR. PRESS. DROP (IN. WATER)               .095          MIN. FLUID VEL. (FT/SEC)                    1.330
TOTAL PRESS. DROP (IN. WATER)                .372          HOLES/IN.**2 IN DISTR. PLATE                3.636
OUTLET PRESSURE (PSIA)                     14.687          PARTICLE TERMINAL VEL. (FT/SEC)            16.059
WEIGHT OF SORBENT (LBS)                 24493.668          SUPERFICIAL VELOCITY (FT/SEC)               5.318
FRACTION OF SOLIDS IN CLOUD                -7.392          FRACTIONS OF BUBBLES IN BED                  .978
FRACTION OF SOLIDS IN EMULSION              7.527
```

TABLE IV (Continued)

```
PAGE  3                                                               28 APR 19
                              INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)          146.940         SHELL HEIGHT (FEET)                   73.470
  SHELL THICKNESS (INCHES)                 .454         CURRENT COST INDEX                   272.200


                             OUTPUT PARAMETERS FOR SORBER SHELL


  WEIGHT OF SHELL (LBS)             1467569.800         LINING COST (DOLLARS)                 24167.
  WEIGHT OF HEADS (LBS)             1467569.800         COST OF VESSEL (DOLLARS)             631302.
  WEIGHT OF DISTR. PLATE (LBS)       503211.650         TOTAL COST OF SORBER (DOLLARS)       655470.
  WEIGHT OF VESSEL (LBS)            3438351.200
```

TABLE IV (Continued)

```
PAGE  5                                                           28 APR 19
                          INPUT PARAMETERS FOR CYCLONE

CYCLONE REMOVAL EFFICIENCY (%)      98.000     PRESSURE DROP (INCHES WATER)         5.000
FLUID DENSITY (LBS/FT**3)             .036     SOLID DENSITY (LBS/FT**3)          100.000
VISCOSITY (LBS/FT-SEC)           .00002033     WALL THICKNESS (INCHES)               .250
EFFECTIVE TURNS                      3.500     CURRENT COST INDEX                 272.200
INPUT FLOW RATE (ACFM)         5409830.700     NUMBER OF CYCLONES                      2.

                          OUTPUT PARAMETERS FOR CYCLONE

                          INDIVIDUAL CYCLONE PARAMETERS

INPUT FLOW RATE (ACFM)         2704940.400     INLET VELOCITY (FT/SEC)             75.774
CYCLONE DIAMETER (FEET)             68.996     CYCLONE WEIGHT (LBS)            744532.970
PART. SIZE (MICRONS)- 98.% EFF.     71.816     COST OF EACH CYCLONE (DOLLARS)     278901.
PART. SIZE (MICRONS)- 50% EFF.      42.477

TOTAL COST OF ALL CYCLONE UNITS    557803.
```

TABLE IV (Continued)

```
PAGE  7                                                                       28 APR 196

                                INPUT VARIABLES FOR FAN COST

  COST INDEX AS OF JANUARY 1969          272.200      TOTAL FAN CAPACITY (ACFM)          5409880.700
  FAN SPEED (RPM)                       1200.000      AIR DENSITY (LBS/FT**3)                   .036
  OVERALL EFFICIENCY                        .850      FAN PRESSURE DROP (IN. WATER)            5.372
  NUMBER OF FAN UNITS                         1.


                            FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                INDIVIDUAL FAN UNIT PARAMETERS

  FAN CAPACITY (ACFM)                5409880.700      WHEEL DIAMETER (INCHES)                 74.644
  DRIVER BRAKE HORSEPOWER               5368.083      FAN COST (DOLLARS)                      25330.
  ACTUAL DRIVER HORSEPOWER              7792.379      MOTOR COST (DOLLARS)                    77832.
  FRACTIONAL CAPACITY PER FAN              1.000      EACH FAN UNIT COST (DOLLARS)           103163.

  KILOWATTS REQUIRED BY DRIVER(S)       4003.045      COST - ALL FAN UNITS (DOLLARS)         103163.
```

TABLE IV (Continued)

SO2 REMOVAL FROM FLUE GAS
CATEGORY
DRY METAL OXIDES
CAPITAL COST ESTIMATE SUMMARY
CASE NO. 52.

NAME OF PROCESS
TRACOR

NAME OF EQUIPMENT
SORPTION UNIT

FLUE GAS RATE 2.5 MMSCFM

MW 1400.0

	ITEM	COST- THOU. $	% OF TOTAL
1.	PURCHASED EQUIPMENT	1316.4	19.22
2.	ERECTION LABOR	329.1	4.80
3.	FOUNDATION & PLATFORMS	237.0	3.46
4.	PIPING	987.3	14.41
5.	INSTRUMENTS	197.5	2.89
6.	INSULATION	105.3	1.54
7.	ELECTRICAL	131.6	1.92
8.	BUILDINGS	329.1	4.80
9.	LAND & YARD IMPROVEMENTS	171.1	2.50
10.	UTILITIES	526.6	7.69
11.	PHYSICAL-PLANT COST	4331.1	63.23
12.	ENGINEERING & CONSTRUCTION	868.8	12.68
13.	DIRECT PLANT COST	5199.9	75.92
14.	CONTRACTOR-S FEE	250.1	3.65
15.	CONTINGENCY	776.7	11.34
16.	FIXED CAPITAL COST	6226.7	90.91
17.	WORKING CAPITAL	622.7	9.09
	TOTAL INVESTMENT	6849.4	100.00
18.	CAPITAL REQUIREMENTS $/KW CAPACITY	4.9	

TABLE IV (Continued)

```
                     SO2 REMOVAL FROM FLUE GAS
                              CATEGORY
                          DRY METAL OXIDES

                    OPERATING COST ESTIMATE SUMMARY
                 BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

           NAME OF PROCESS                        NAME OF EQUIPMENT
               TRACOR                              SORPTION UNIT

   FLUE GAS RATE    2.5 MMSCFM                                   MW 1400.0
                       FIXED CAPITAL COST   6226737.6

----------------------------------------------------------------------------------------

                    ITEM                                COST- THOU. $      % OF TOTAL
                    ----                                -------------      ----------

   1.  RAW MATERIALS & CHEMICALS                                  .0             .00
   2.  DIRECT LABOR                                             54.0            5.11
   3.  SUPERVISION                                              27.4            2.59
   4.  MAINTENANCE, 5% OF FIXED CAPITAL                        311.3           29.43
   5.  SUPPLIES, 15% OF MAINTENANCE                             46.7            4.42
   6.  UTILITIES                                               133.2           12.60
   7.  OTHER                                                      .0             .00
   8.       TOTAL DIRECT COST                                  572.7           54.14
   9.  PAYROLL BURDEN, 20% OF 2 & 3                             16.3            1.54
  10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                      219.7           20.77
  11.  PACK & SHIP                                                .0             .00
  12.  WASTE DISPOSAL                                             .0             .00
  13.  OTHER                                                      .0             .00
  14.       TOTAL INDIRECT COST                                236.0           22.31
  15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                   62.3            5.89
  16.  TAXES, 2% OF FIXED CAPITAL                              124.5           11.77
  17.  INSURANCE, 1% OF FIXED CAPITAL                           62.3            5.89
  18.  OTHER                                                      .0             .00
  19.       TOTAL FIXED COST                                   249.1           23.55

  20.  TOTAL OPERATING COST                                   1057.7          100.00
  21.  COST:  $/TON OF COAL                  .230
                 MIL/KWH                     .095
```

TABLE IV (Continued)

```
PAGE  1                                                                          28 APR 196

                                   INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                    500000.000        DENSITY OF SOLID (LBS/FT**3)        100.000
PARTICLE DIAMETER (INCHES)              .0450        INLET CONCENT. (MOLE PERCENT)        .00300
REACTION RATE (1/SEC)               135.00000        OUTLET CONCENT. (MOLE PERCENT)       .00015
RATIO- SUPERFICIAL TO MIN. VEL.         4.000        VOL. WAKE / VOL. BUBBLE                .320
TEMPERATURE (DEG. F.)                 666.000        FRACTION OF SOLIDS IN BUBBLE           .000
INLET PRESSURE (PSIA)                  14.700


                                  OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                   1081976.100        INITIAL BUBBLE DIAMETER (FEET)         .194
DIAMETER OF BED (FEET)                 65.714        FINAL BUBBLE DIAMETER (FEET)           .328
HEIGHT OF BED (FEET)                    1.214        INITIAL BUBBLE VEL. (FT/SEC)          5.763
HEIGHT OF VESSEL (FEET)                32.857        FINIAL BUBBLE VEL. (FT/SEC)           6.298
THICKNESS OF SHELL (INCHES)              .238        MIN. MASS FLUX (LBS/HR-FT**2)       173.838
BED PRESSURE DROP (IN. WATER)            .277        MIN. FLUID VOIDAGE                     .450
DISTR. PRESS. DROP (IN. WATER)           .095        MIN. FLUID VEL. (FT/SEC)              1.330
TOTAL PRESS. DROP (IN. WATER)            .372        HOLES/IN.**2 IN DISTR. PLATE          3.636
OUTLET PRESSURE (PSIA)                 14.687        PARTICLE TERMINAL VEL. (FT/SEC)      16.059
WEIGHT OF SORBENT (LBS)              4898.733        SUPERFICIAL VELOCITY (FT/SEC)         5.318
FRACTION OF SOLIDS IN CLOUD            -7.392        FRACTIONS OF BUBBLES IN BED            .978
FRACTION OF SOLIDS IN EMULSION          7.527
```

TABLE IV (Continued)

```
PAGE  3                                                                      28 APR 198
                              INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)        65.714        SHELL HEIGHT (FEET)                  32.857
  SHELL THICKNESS (INCHES)              .238        CURRENT COST INDEX                  272.200


                            OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (LBS)           153583.880        LINING COST (DOLLARS)                 4833.
  WEIGHT OF HEADS (LBS)           153583.870        COST OF VESSEL (DOLLARS)             96860.
  WEIGHT OF DISTR. PLATE (LBS)    100642.328        TOTAL COST OF SORBER (DOLLARS)      101694.
  WEIGHT OF VESSEL (LBS)          407810.080
```

TABLE IV (Continued)

```
PAGE  4                                                                              28 APR 19
                                  INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (CM)            2002.855        SHELL HEIGHT (CM)                    1001.427
  SHELL THICKNESS (CM)                      .604        CURRENT COST INDEX                    272.200


                                  OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (GM)              69652551.000        LINING COST (DOLLARS)                   4833.
  WEIGHT OF HEADS (GM)              69652550.000        COST OF VESSEL (DOLLARS)               96860.
  WEIGHT OF DISTR. PLATE (GM)       45642780.000        TOTAL COST OF SORBER (DOLLARS)        101694.
  WEIGHT OF VESSEL (GM)            184947880.000
```

TABLE IV (Continued)

```
PAGE  5                                                                                    28 APR 198
                                         INPUT PARAMETERS FOR CYCLONE

  CYCLONE REMOVAL EFFICIENCY (%)          98.000          PRESSURE DROP (INCHES WATER)            5.000
  FLUID DENSITY (LBS/FT**3)                 .036          SOLID DENSITY (LBS/FT**3)             100.000
  VISCOSITY (LBS/FT-SEC)               .00002083          WALL THICKNESS (INCHES)                  .250
  EFFECTIVE TURNS                          3.500          CURRENT COST INDEX                    272.200
  INPUT FLOW RATE (ACFM)             1081976.100          NUMBER OF CYCLONES                         2.


                                         OUTPUT PARAMETERS FOR CYCLONE


                                         INDIVIDUAL CYCLONE PARAMETERS

  INPUT FLOW RATE (ACFM)              540988.070          INLET VELOCITY (FT/SEC)                75.774
  CYCLONE DIAMETER (FEET)                 30.856          CYCLONE WEIGHT (LBS)               148906.600
  PART. SIZE (MICRONS)- 98.% EFF.         48.026          COST OF EACH CYCLONE (DOLLARS)          55780.
  PART. SIZE (MICRONS)- 50% EFF.          28.406

  TOTAL COST OF ALL CYCLONE UNITS        111561.
```

TABLE IV (Continued)

```
PAGE  7                                                                          28 APR 196

                                  INPUT VARIABLES FOR FAN COST

   COST INDEX AS OF JANUARY 1969          272.200        TOTAL FAN CAPACITY (ACFM)          1081976.100
   FAN SPEED (RPM)                       1200.000        AIR DENSITY (LBS/FT**3)                   .036
   OVERALL EFFICIENCY                        .850        FAN PRESSURE DROP (IN. WATER)            5.372
   NUMBER OF FAN UNITS                         1.


                           FAN AND DRIVER MOTOR OUTPUT PARAMETERS

                                 INDIVIDUAL FAN UNIT PARAMETERS

   FAN CAPACITY (ACFM)                1081976.100        WHEEL DIAMETER (INCHES)                 62.331
   DRIVER BRAKE HORSEPOWER               1073.617        FAN COST (DOLLARS)                      15967.
   ACTUAL DRIVER HORSEPOWER              1558.476        MOTOR COST (DOLLARS)                    16871.
   FRACTIONAL CAPACITY PER FAN              1.000        EACH FAN UNIT COST (DOLLARS)            32838.

   KILOWATTS REQUIRED BY DRIVER(S)        800.609        COST - ALL FAN UNITS (DOLLARS)          32838.
```

TABLE IV (Continued)

SO2 REMOVAL FROM FLUE GAS
CATEGORY
DRY METAL OXIDES
CAPITAL COST ESTIMATE SUMMARY
CASE NO. 51.

NAME OF PROCESS
TRACOR

NAME OF EQUIPMENT
SORPTION UNIT

FLUE GAS RATE .5 MMSCFM

MW 1400.0

	ITEM	COST- THOU. $	% OF TOTAL
1.	PURCHASED EQUIPMENT	246.1	19.22
2.	ERECTION LABOR	61.5	4.80
3.	FOUNDATION & PLATFORMS	44.3	3.46
4.	PIPING	184.6	14.41
5.	INSTRUMENTS	36.9	2.88
6.	INSULATION	19.7	1.54
7.	ELECTRICAL	24.6	1.92
8.	BUILDINGS	61.5	4.80
9.	LAND & YARD IMPROVEMENTS	32.0	2.50
10.	UTILITIES	98.4	7.69
11.	PHYSICAL-PLANT COST	809.6	63.23
12.	ENGINEERING & CONSTRUCTION	162.4	12.68
13.	DIRECT PLANT COST	972.1	75.92
14.	CONTRACTOR-S FEE	46.8	3.65
15.	CONTINGENCY	145.2	11.34
16.	FIXED CAPITAL COST	1164.0	90.91
17.	WORKING CAPITAL	116.4	9.09
	TOTAL INVESTMENT	1280.4	100.00
18.	CAPITAL REQUIREMENTS $/KW CAPACITY	.9	

TABLE IV (Continued)

```
PAGE 10                                                                                     28 APR 19
                                   SO2 REMOVAL FROM FLUE GAS
                                           CATEGORY
                                       DRY METAL OXIDES

                                OPERATING COST ESTIMATE SUMMARY
                              BASIS:  330 DAY/YEAR &   70.0 % CAPACITY

                       NAME OF PROCESS                         NAME OF EQUIPMENT
                           TRACOR                               SORPTION UNIT

           FLUE GAS RATE     .5 MMSCFM                                         MW 1400.0
                                   FIXED CAPITAL COST   1154016.9

-------------------------------------------------------------------------------------------------

                         ITEM                                       COST- THOU. $        % OF TOTAL
                         ----                                       -------------        ----------

        1.  RAW MATERIALS & CHEMICALS                                          .0              .00
        2.  DIRECT LABOR                                                     54.0            17.31
        3.  SUPERVISION                                                      27.4             8.78
        4.  MAINTENANCE, 5% OF FIXED CAPITAL                                 58.2            18.66
        5.  SUPPLIES, 15% OF MAINTENANCE                                      8.7             2.80
        6.  UTILITIES                                                        26.6             8.54
        7.  OTHER                                                              .0              .00
        8.       TOTAL DIRECT COST                                          175.0            56.09
        9.  PAYROLL BURDEN, 20% OF 2 & 3                                     16.3             5.22
       10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                               74.2            23.77
       11.  PACK & SHIP                                                        .0              .00
       12.  WASTE DISPOSAL                                                     .0              .00
       13.  OTHER                                                              .0              .00
       14.       TOTAL INDIRECT COST                                         90.4            28.99
       15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                           11.6             3.73
       16.  TAXES, 2% OF FIXED CAPITAL                                       23.3             7.46
       17.  INSURANCE, 1% OF FIXED CAPITAL                                   11.6             3.73
       18.  OTHER                                                              .0              .00
       19.       TOTAL FIXED COST                                            46.6            14.92

       20.  TOTAL OPERATING COST                                            312.0           100.00
       21.  COST:  $/TON OF COAL                      .068
                   MIL/KWH                            .023
```

$$F_s \alpha' = Q(C_{in} - C_{out}) \rho_{so_2} \qquad (11)$$

or

$$F_s = \frac{Q(C_{in} - C_{out}) \rho_{so_2}}{\alpha'} \qquad (12)$$

The regeneration equipment will be sized and cost estimated using techniques similar to those used on the sorption unit. The regenerator contactor will be a fluidized bed similar to the sorber except smaller in size.

The total capital investment cost and gross annual operating cost for the dry metal oxide sulfur oxide removal process will be the sum of the costs for the sorption step, regeneration step, sulfur recovery step and an estimated sorbent attrition loss. The net annual operating cost will be the gross annual operating cost with a by-product credit given for the sulfur product recovered.

IV. SUMMARY AND CONCLUSIONS

The experimental program consisting of compound preparation gathering of kinetic data, and characterization of the compounds using x-ray diffraction and BET surface areas is approximately 75% complete. At this point in time the kinetic data are being incorporated into the economic feasibility studies.

The potential sorbents selected from the thermodynamic screening are being screened kinetically as well as economically. A metal oxide having a reaction rate constant, K_R, greater than 10 cm^3 gas/cm^3 solid-sec is an economically feasible sorbent. Copper oxide (CuO) yielded a reaction rate constant of 135 cm^3 gas/cm^3 solid-sec at 352°C for the sorption step. Using copper oxide as a sorbent for removing SO_2 from furnace flue gases for a 1400 MW power plant processing 2.5 million SCFM of flue gas, the estimated total capital investment would be under $7,000,000, and the gross annual operating cost would be under $1,000,000. These costs compare very favorably with the published economics of other sulfur removal processes. From a kinetic standpoint, several other oxides look very promising. One of the most promising is Cerium oxide which has a reaction rate constant of 70 cm^3 gas/cm^3 solid-sec at a sorption temperature of 262°C.

David W. DeBerry
Terry B. Parsons
Gary D. Schroeder

NOMENCLATURE

C_{in}	Concentration of SO_2 in inlet flue gas stream, mole %
C_{out}	Concentration of SO_2 in outlet flue gas stream, mole %
F_s	Sorbent circulation rate, lb/min
Q	Flow rate of flue gas, ft^3/min
α'	Conversion of sorbent, lb SO_2/ lb sorb
ρ	Density of SO_2, lb/ft^3

BIBLIOGRAPHY

AR-001 R. S. ARIES, P. D. NEWTON, CHEMICAL ENGINEERING COST ESTIMATION, MCGRAW-HILL, NEW YORK, (1955).

HA-002 W. E. HAND, 'FROM FLOW SHEET TO COST ESTIMATE', PETROLEUM REFINER, VOL. 37, NO. 9, PP. 331-4, (1958).

LA-004 H. J. LANG, 'SIMPLIFIED APPROACH TO PRELIMINARY COST ESTIMATION', CHEMICAL ENGINEERING, JUNE (1948).

APPENDIX A

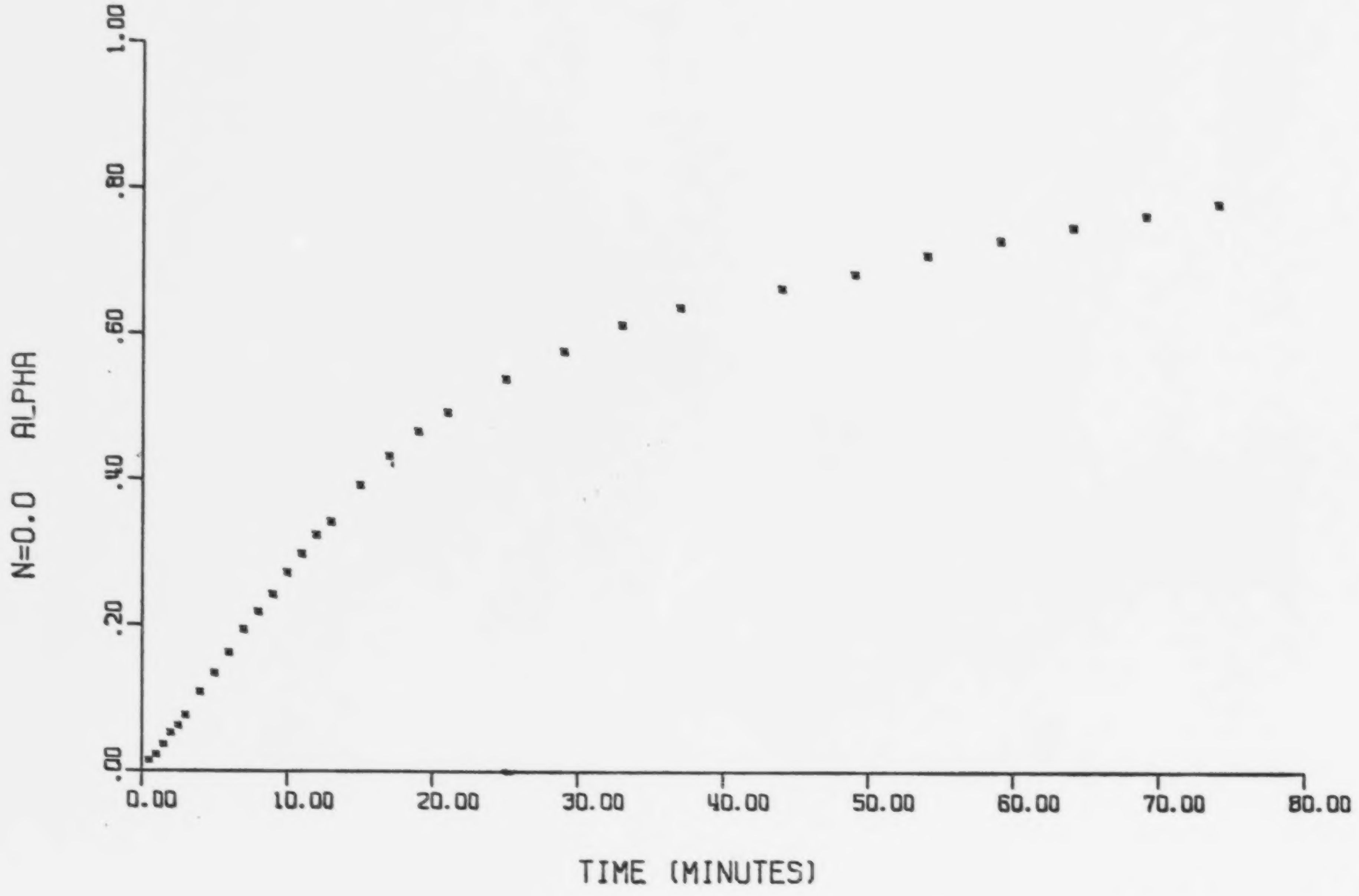
The integrated forms of $f(\alpha)$ are listed below.

n	$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = k't$
0	α
1/3	$3/2\left[1 - (1-\alpha)^{2/3}\right]$
1/2	$2\left[1 - (1-\alpha)^{1/2}\right]$
2/3	$3\left[1 - (1-\alpha)^{1/3}\right]$
1	$-\ln(1-\alpha)$
3/2	$2\left[\frac{1}{(1-\alpha)^{1/2}} - 1\right]$
2	$\frac{\alpha}{1-\alpha}$
DCE	$3/2\left[1 - (1-\alpha)^{2/3}\right] - \alpha$

APPENDIX B

PLOTS FOR DETERMING REACTION RATE CONSTANTS

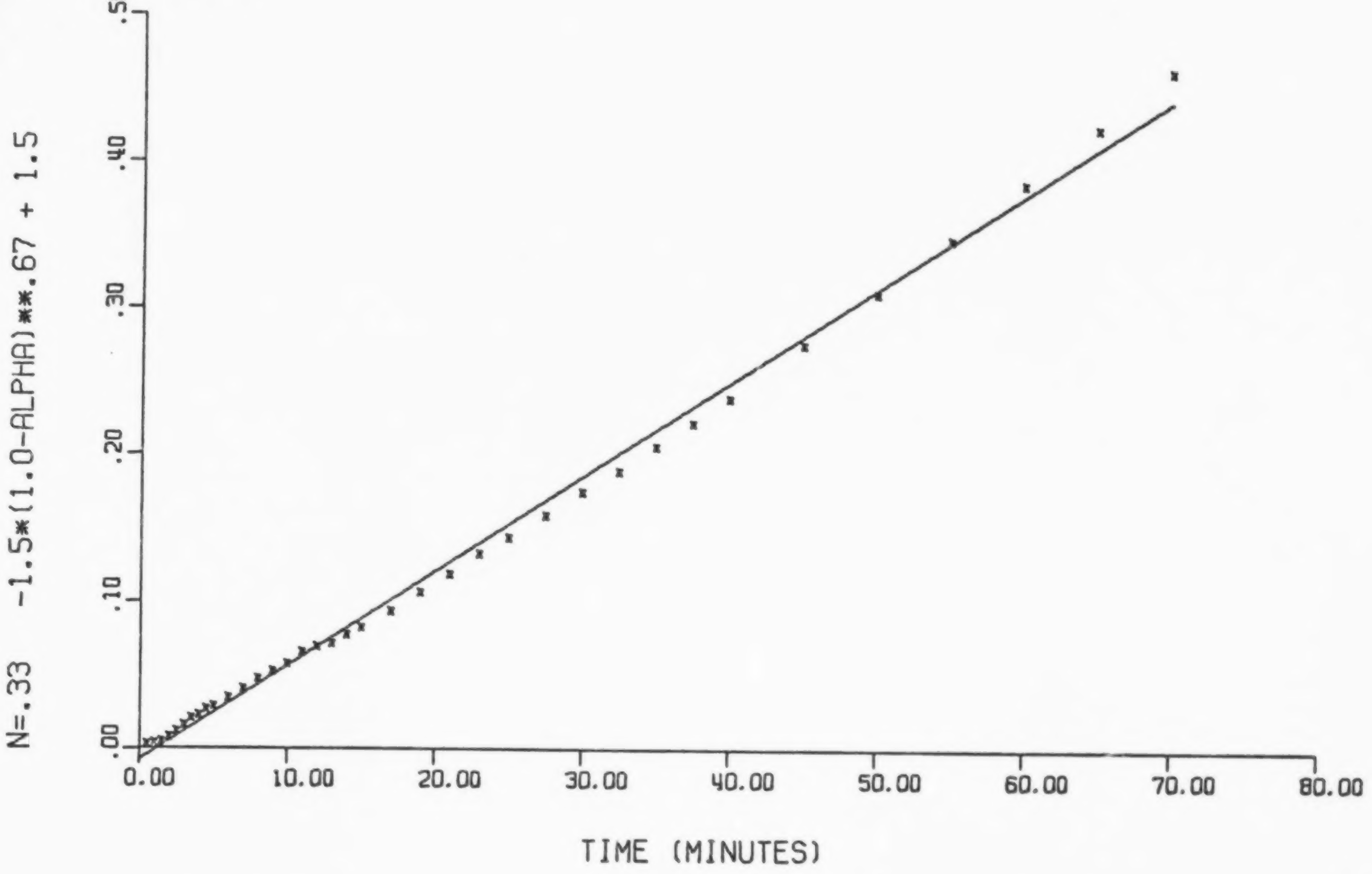
CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



24 MAR 69

TRACOR

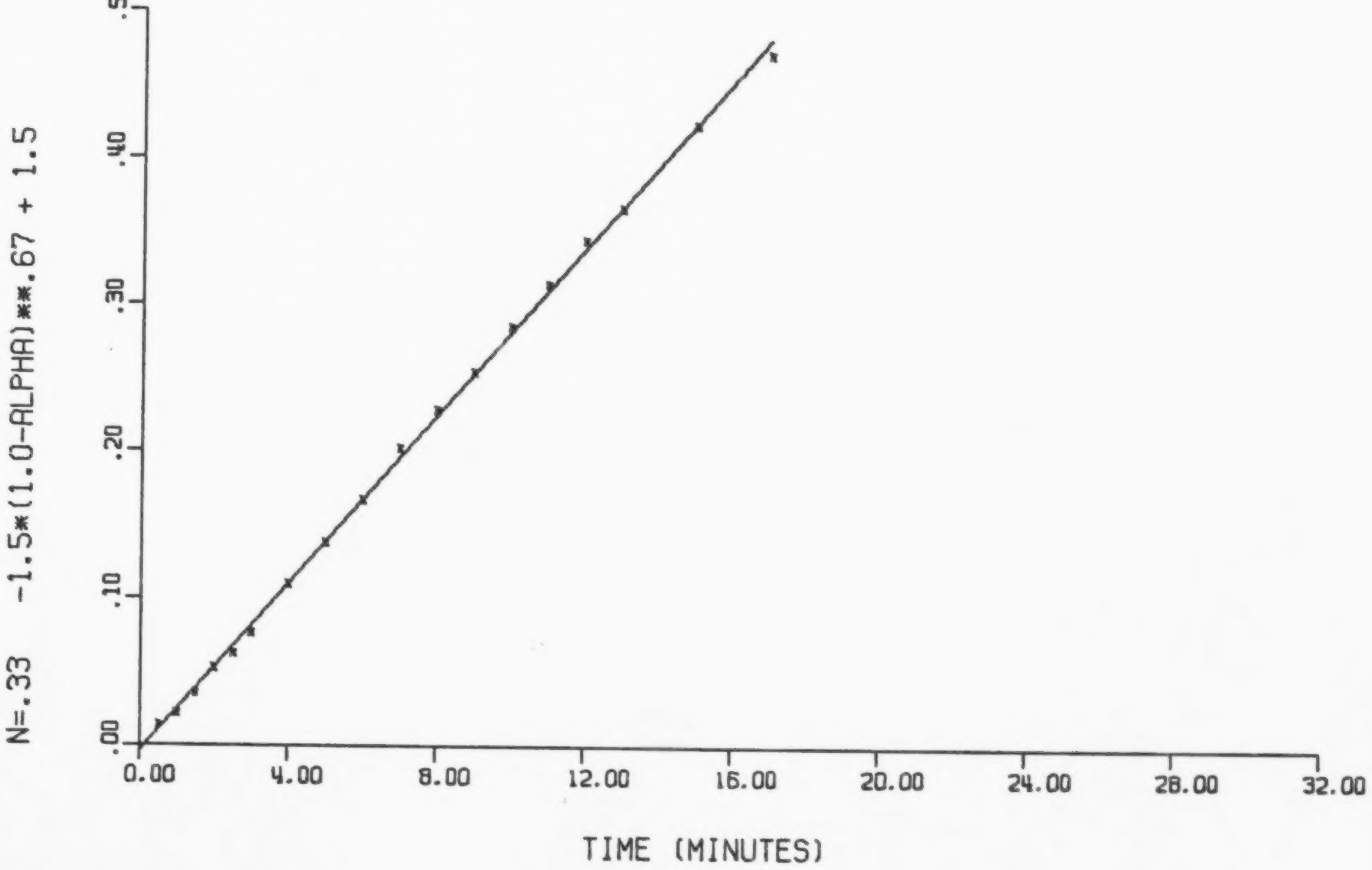
CUO 634-47-1
ISO TGA 4 TEMP = 352 DEG C



18 APR 69

TRACOR

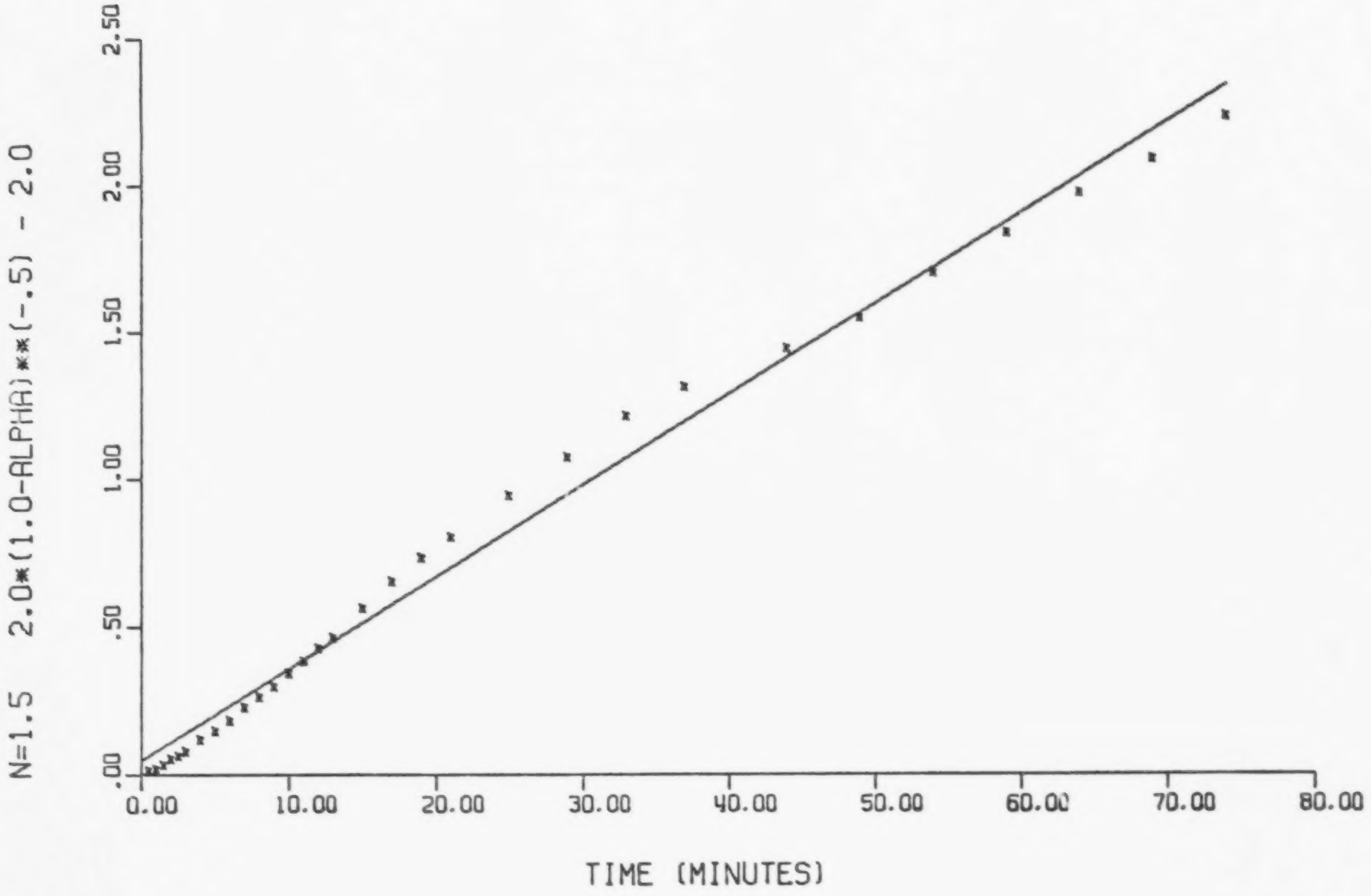
CUO 634-47-1
ISO-TGA-1 TEMP = 404 DEG C



18 APR 69

TRĀCOR

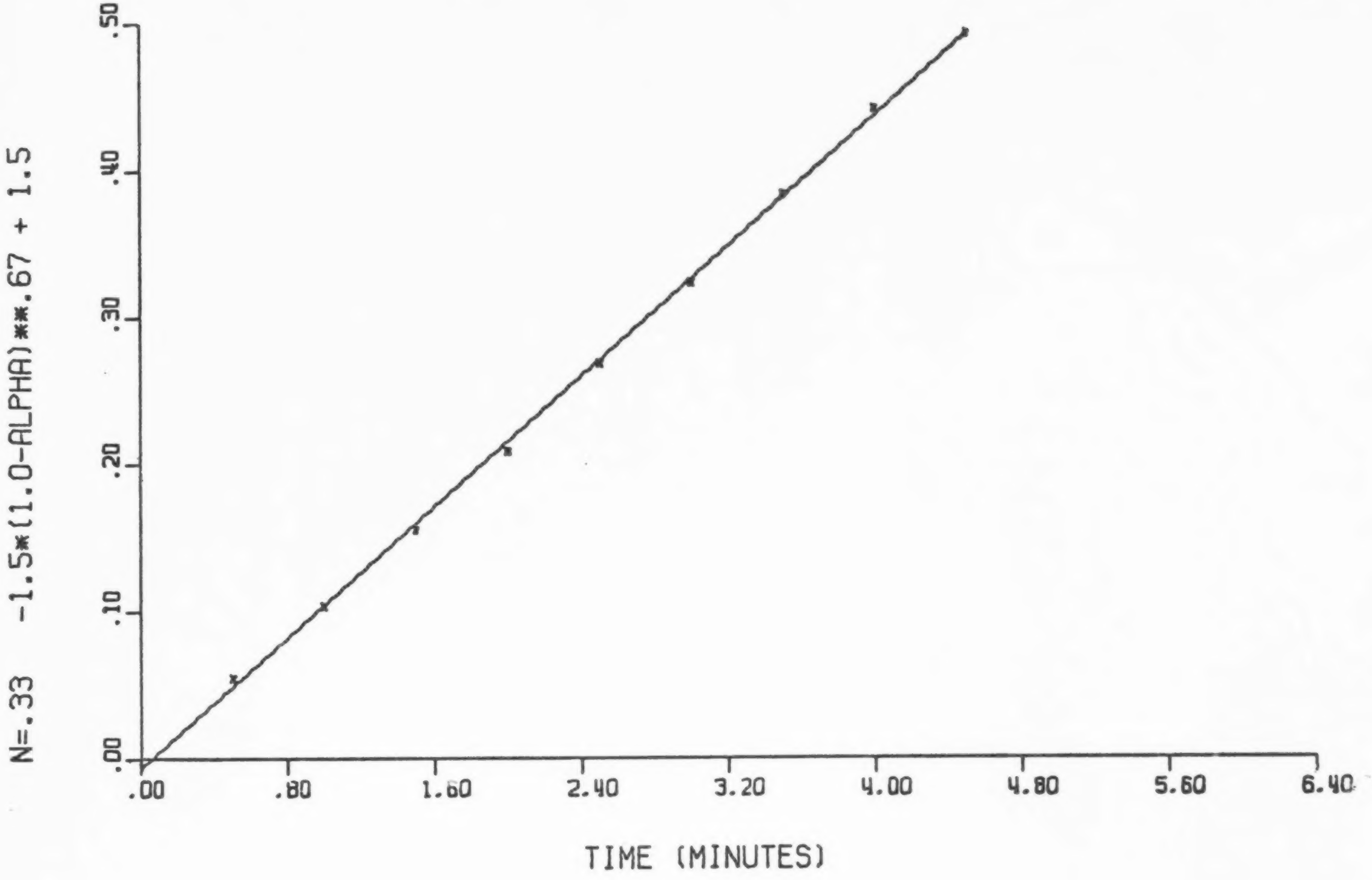
CUO 634-47-1
ISO-TGA-1 TEMP = 404 DEG C



27 MAR 69

CUO 634-47-1   ISO TGA-2

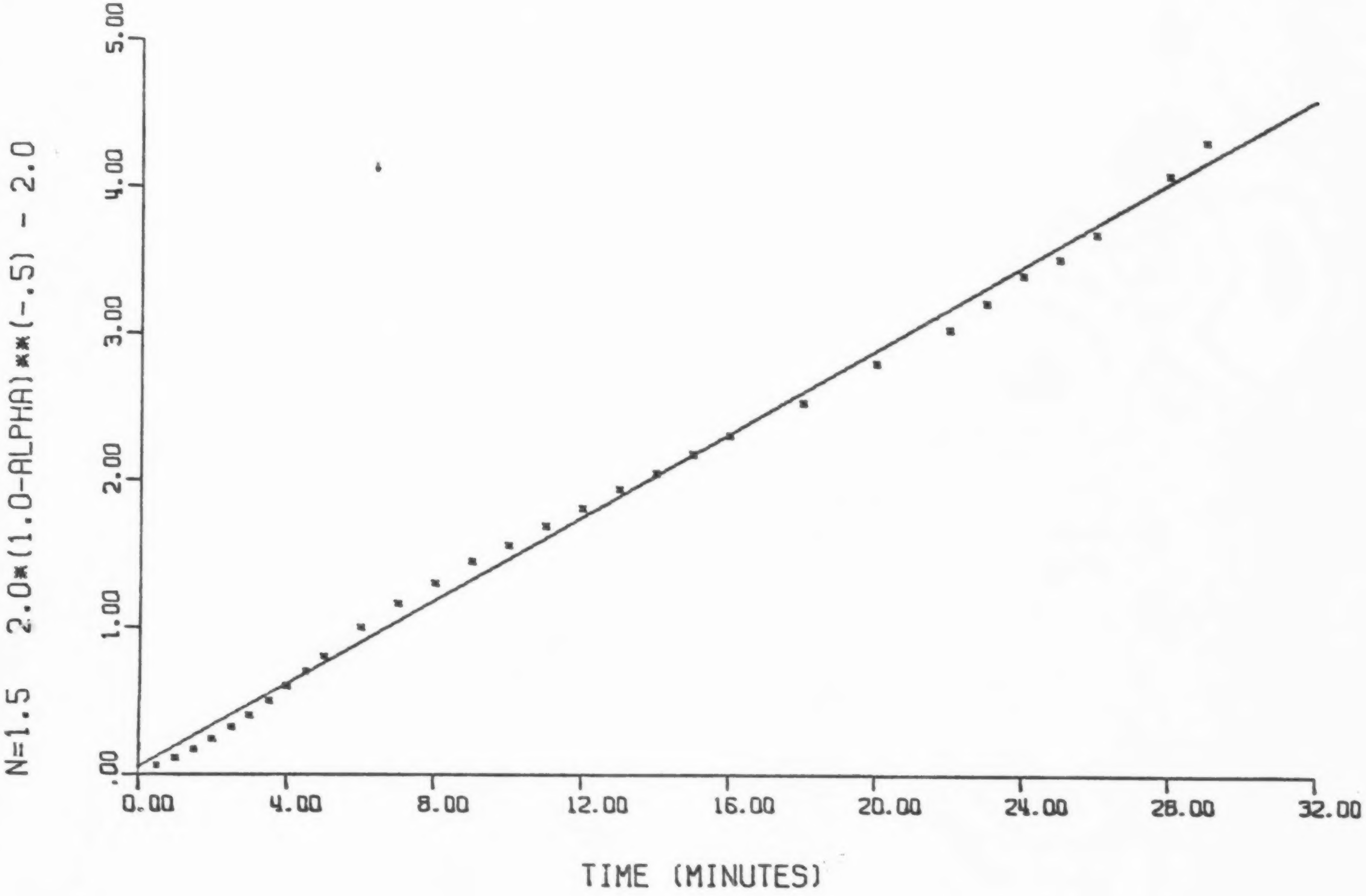
482 DEG ℃



18 APR 69

TRACOR

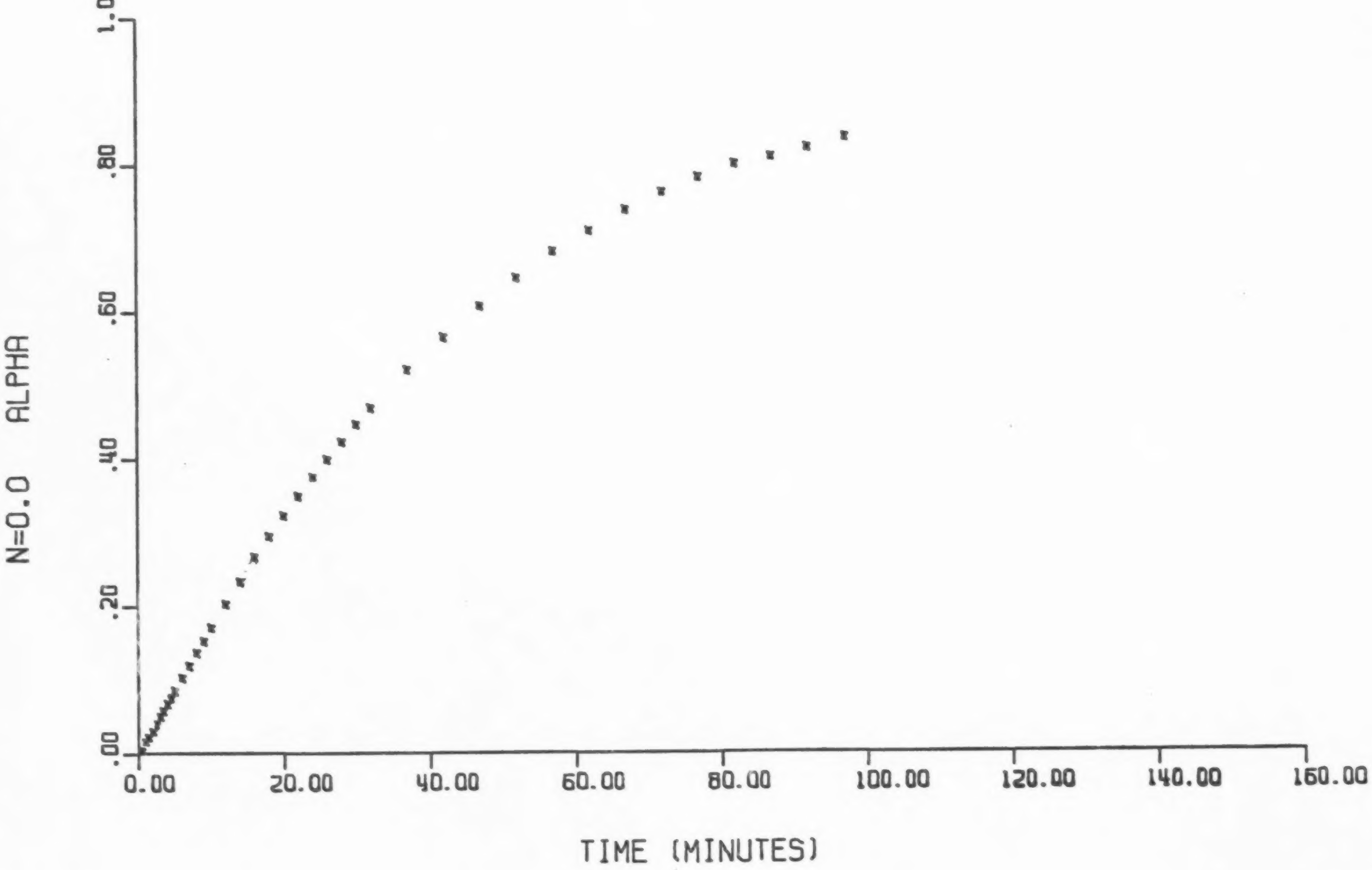
CUO 634-47-1   ISO TGA-2
482 DEG C



24 MAR 69

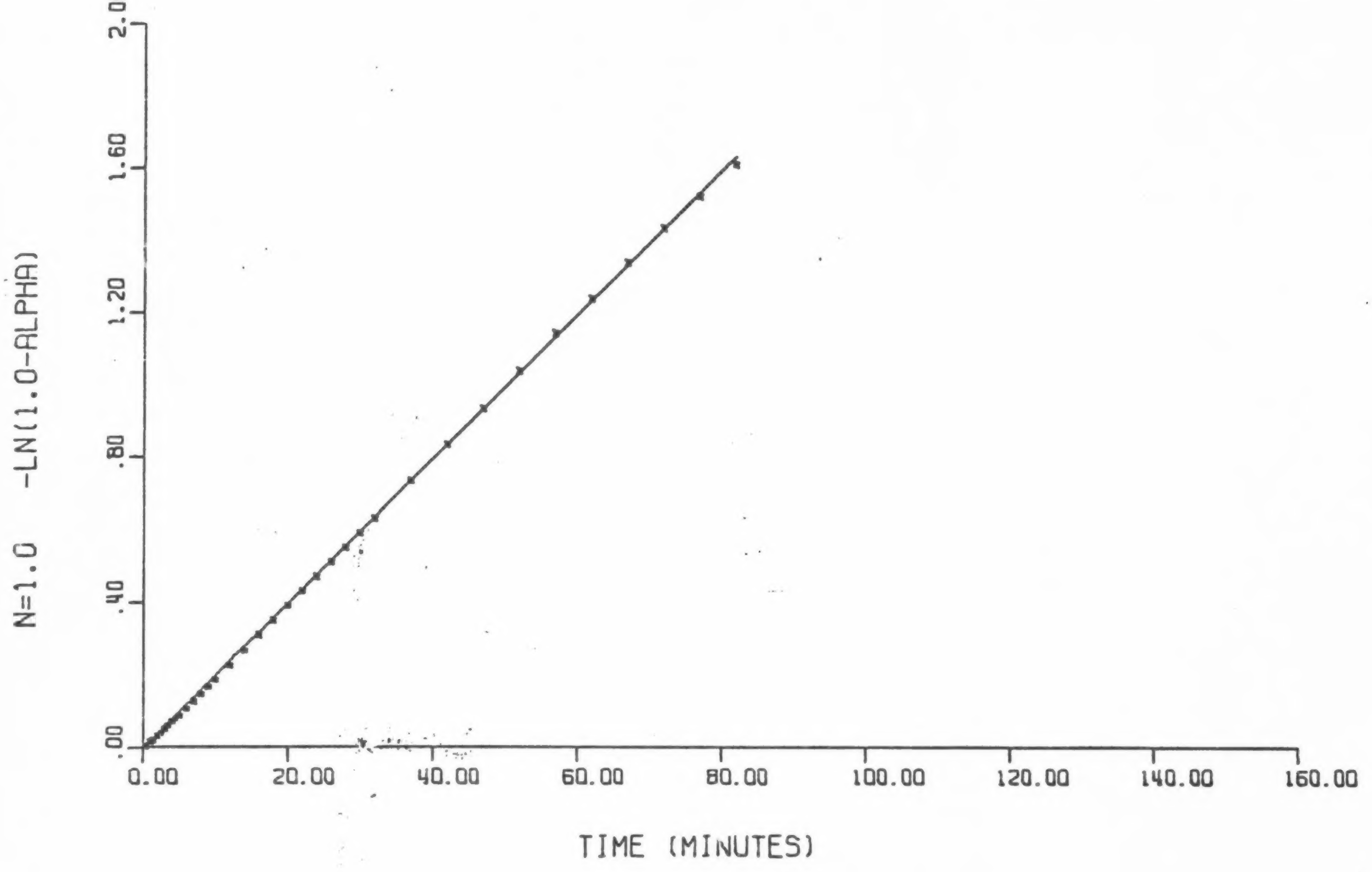
TRACOR

C0304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.



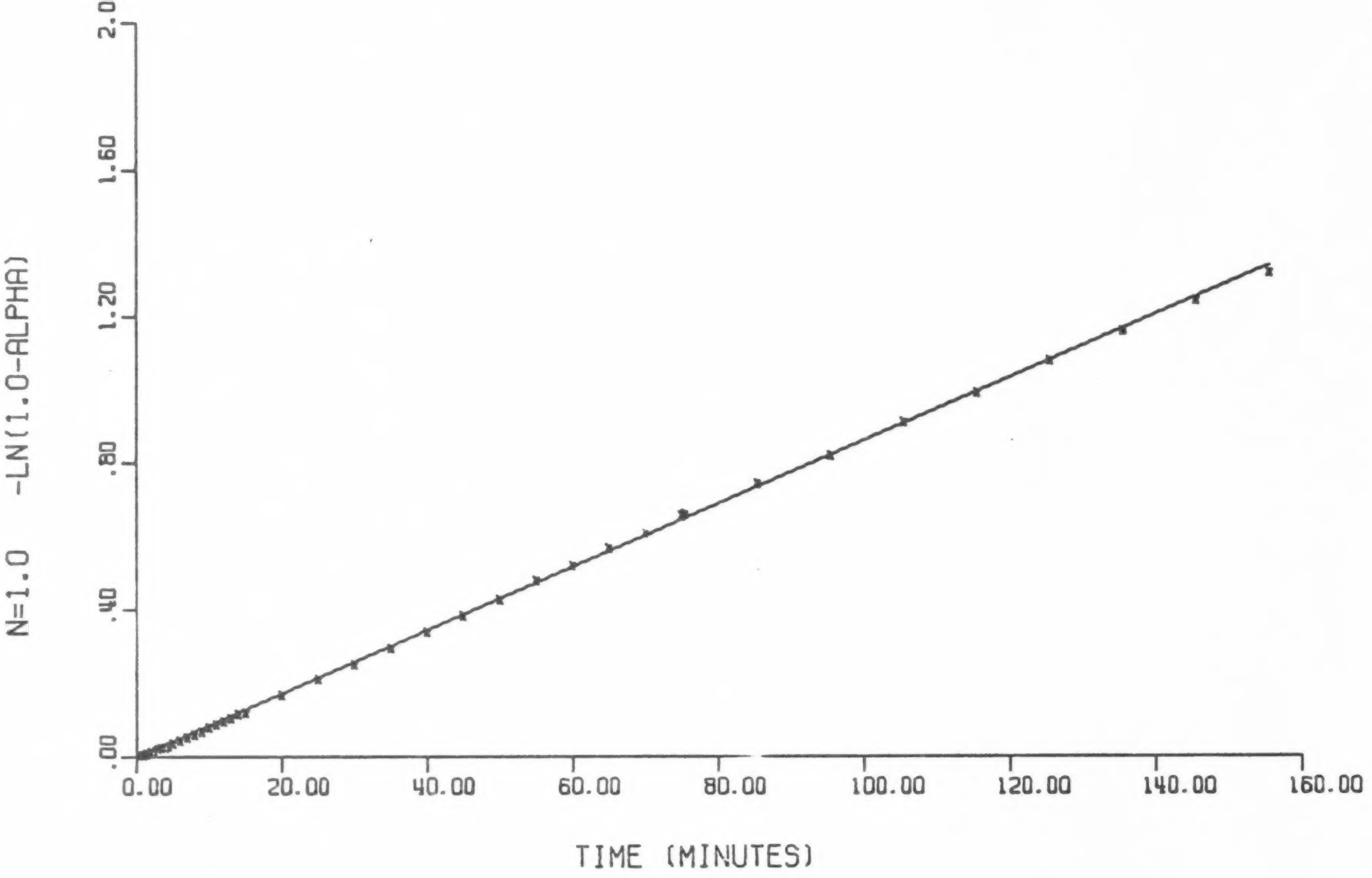
31 MAR 69

CO304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.



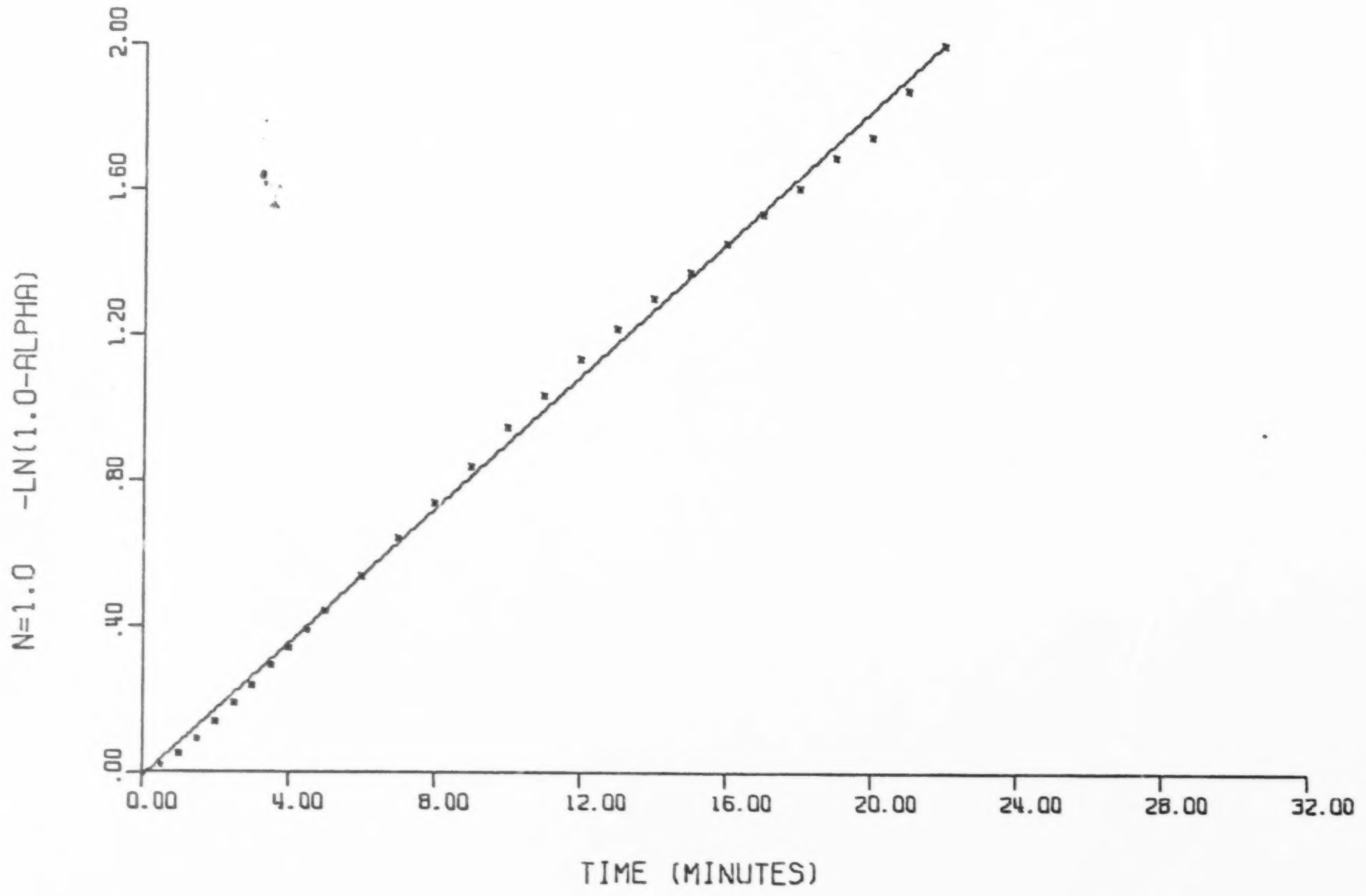
2 APR 69

CO304 634-43-1
SO2 CONC = 0.129 TEMP = 453 DEG C



15 APR 69

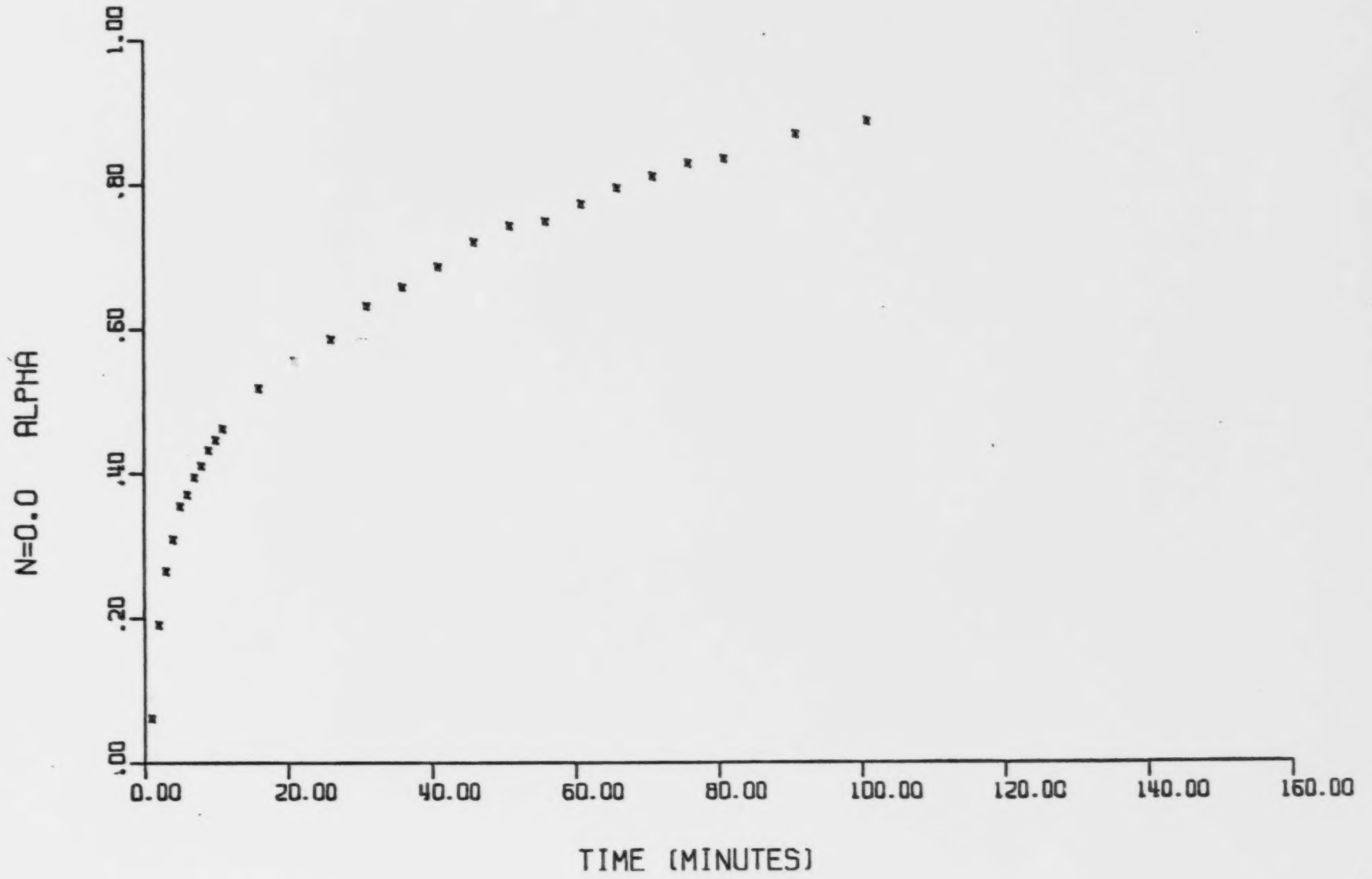
CO3O4 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.



2 APR 69

TRACOR

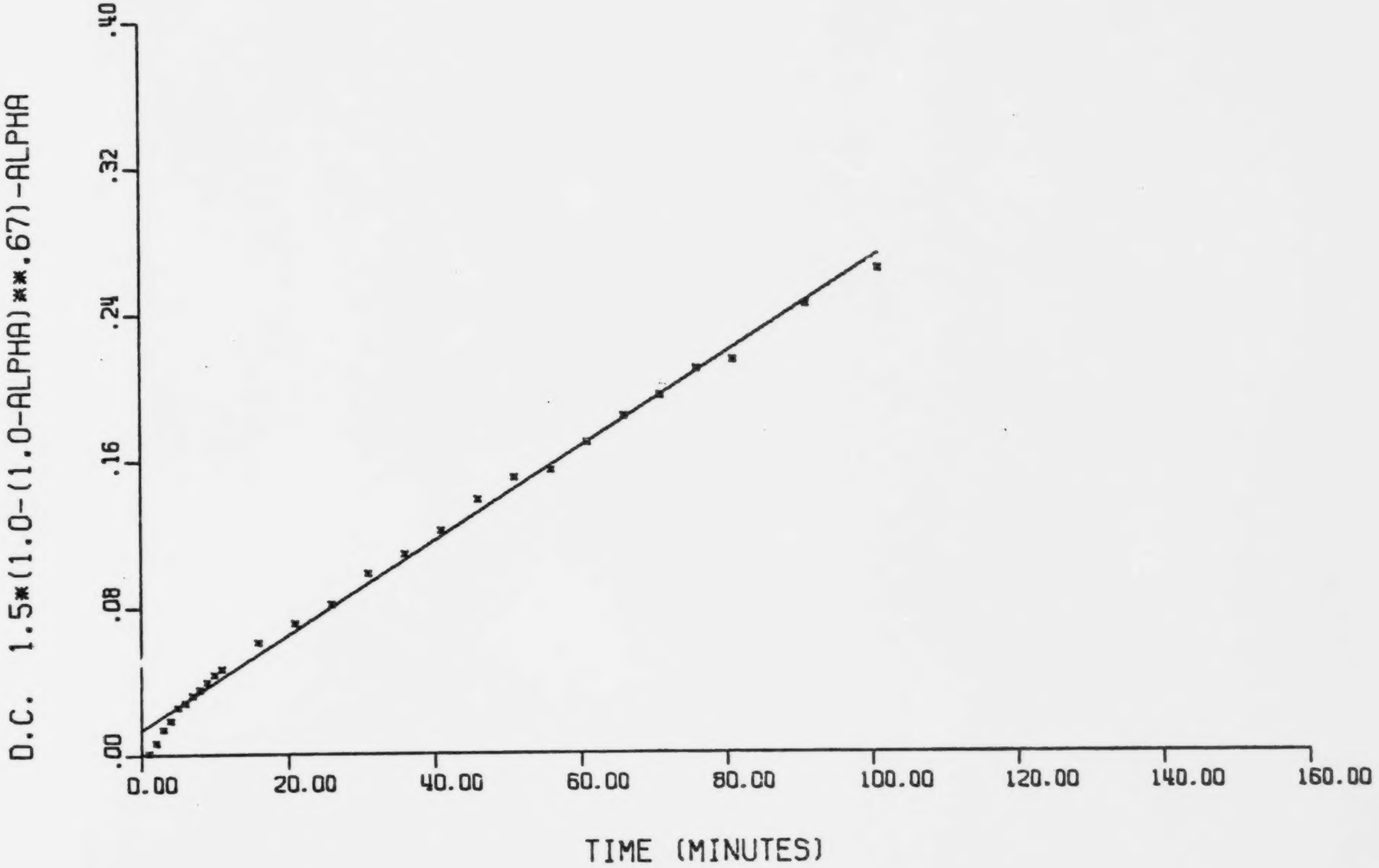
CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

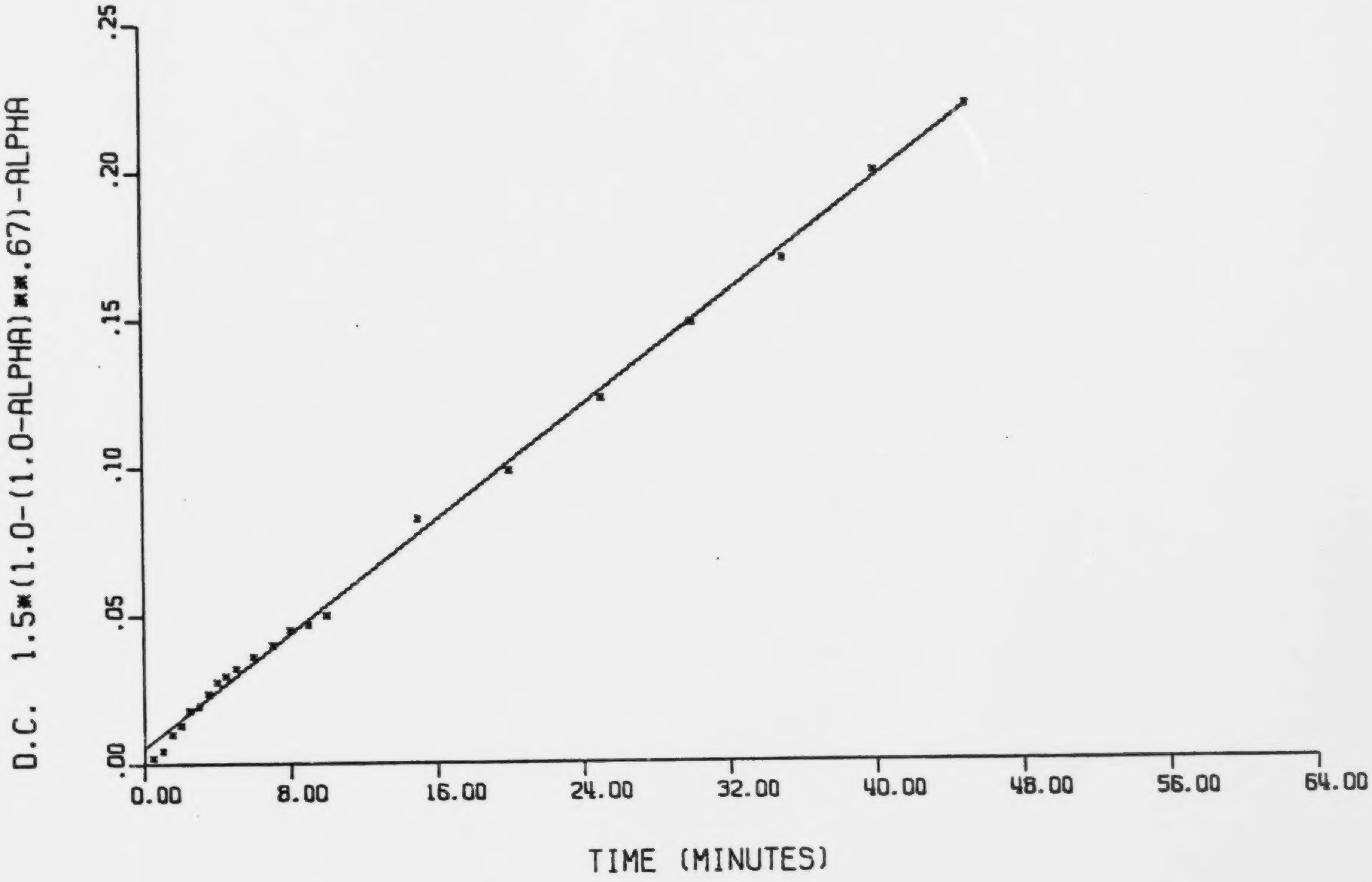
TRACOR

CR2O3 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



14 APR 69

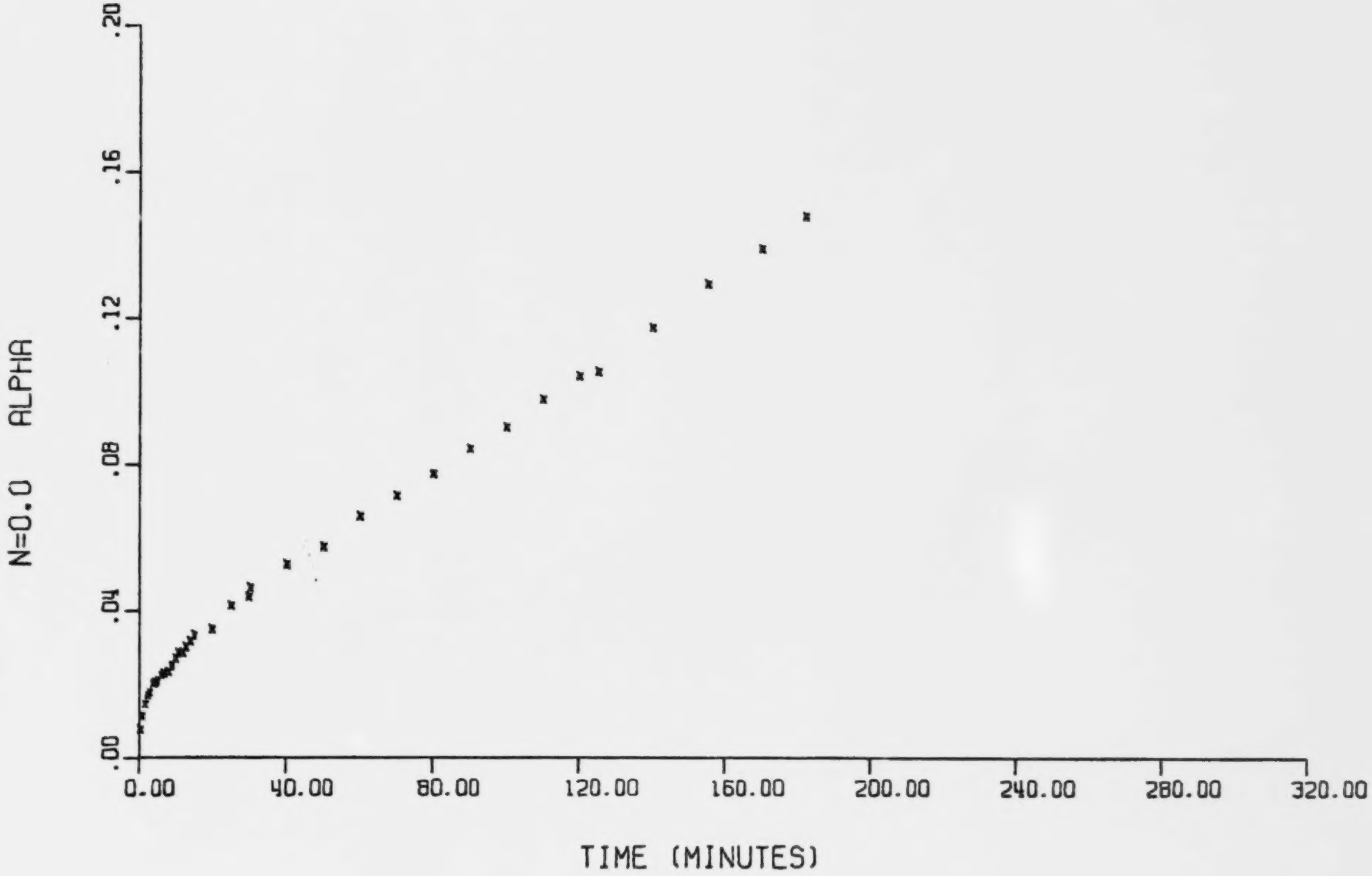
CR203 634-59-2
ISO-TGA-1 TEMP = 390 DEG C.



14 APR 69

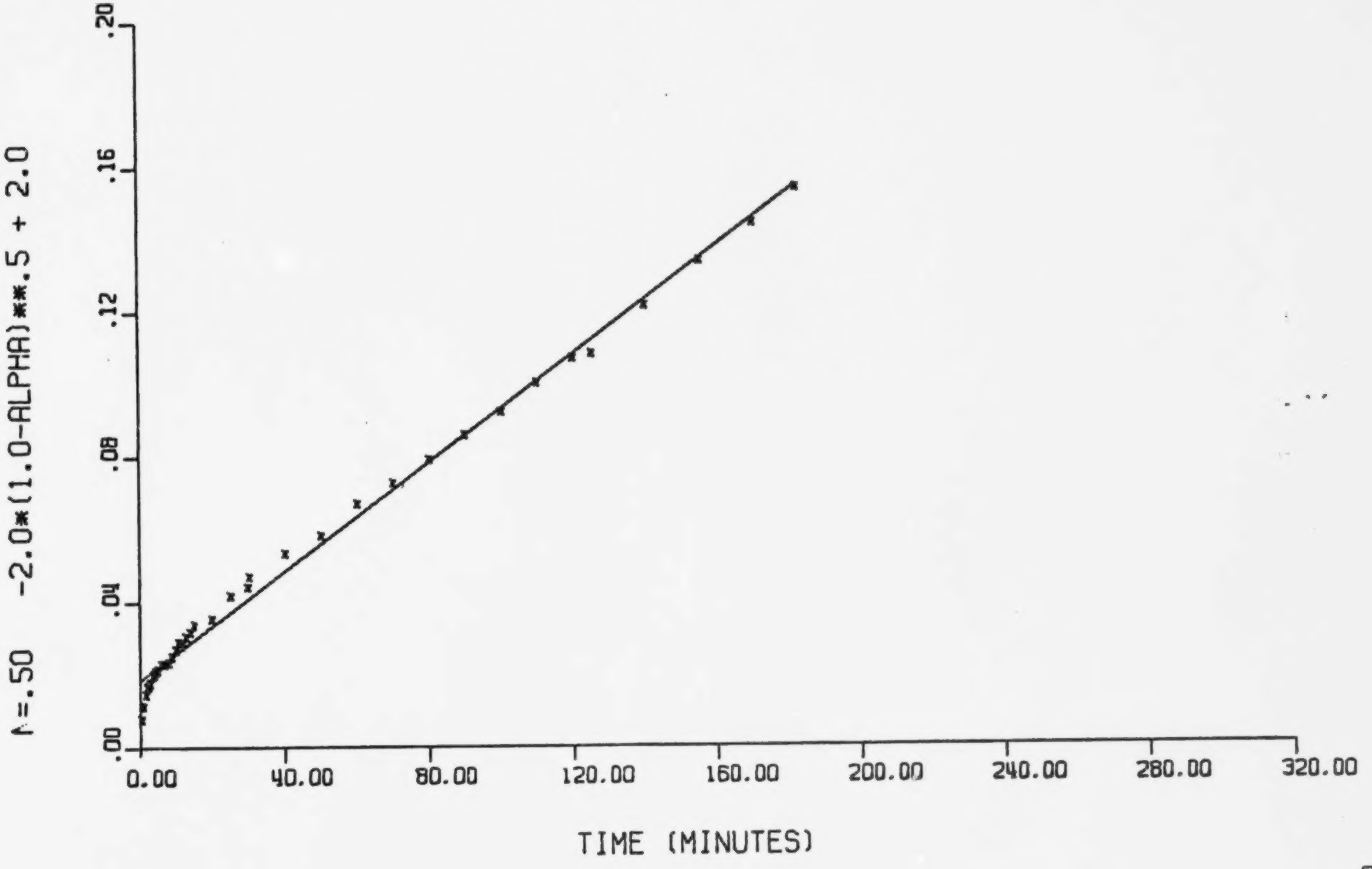
TRACOR

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

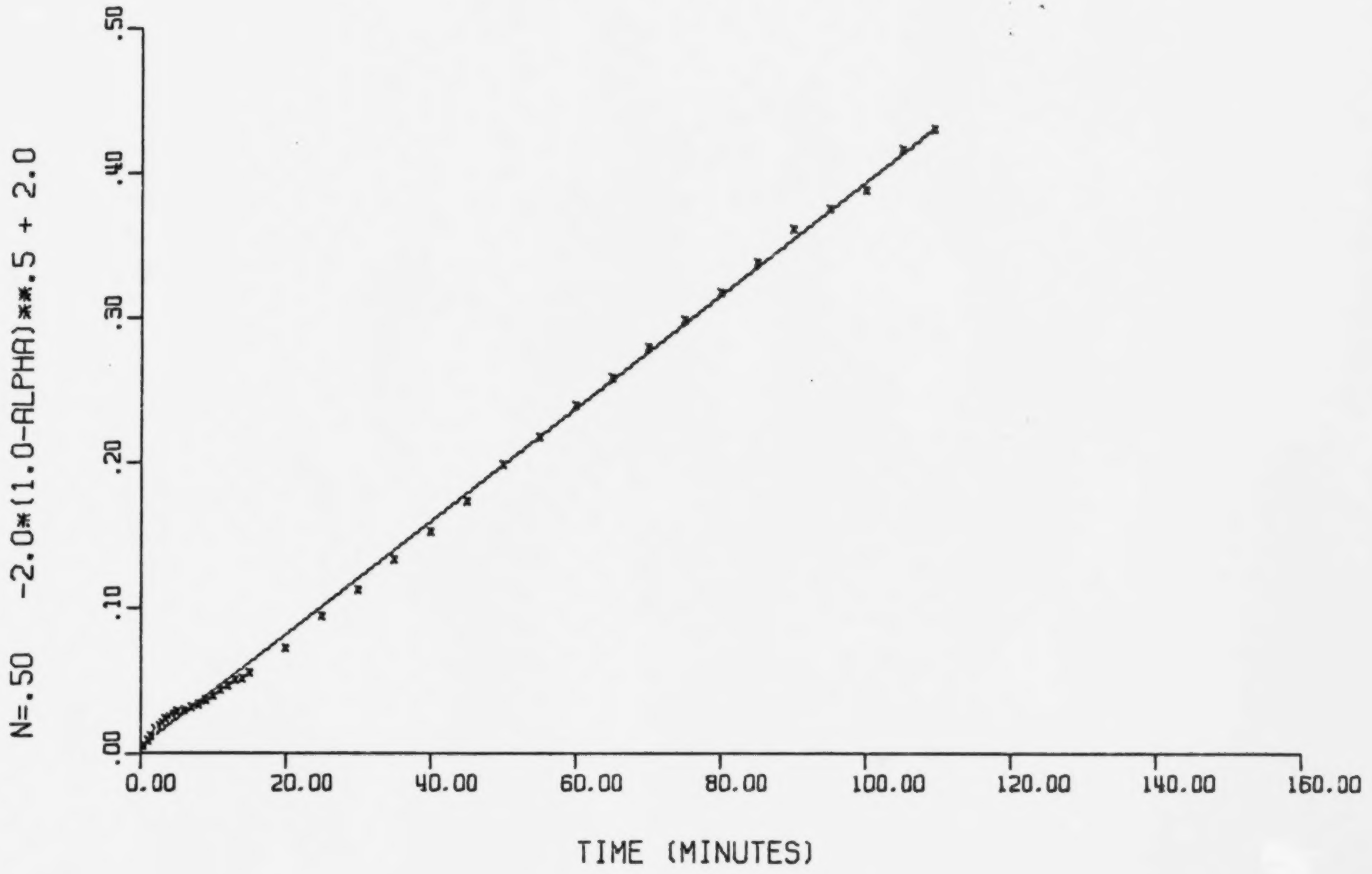
NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



18 APR 69

TRACOR

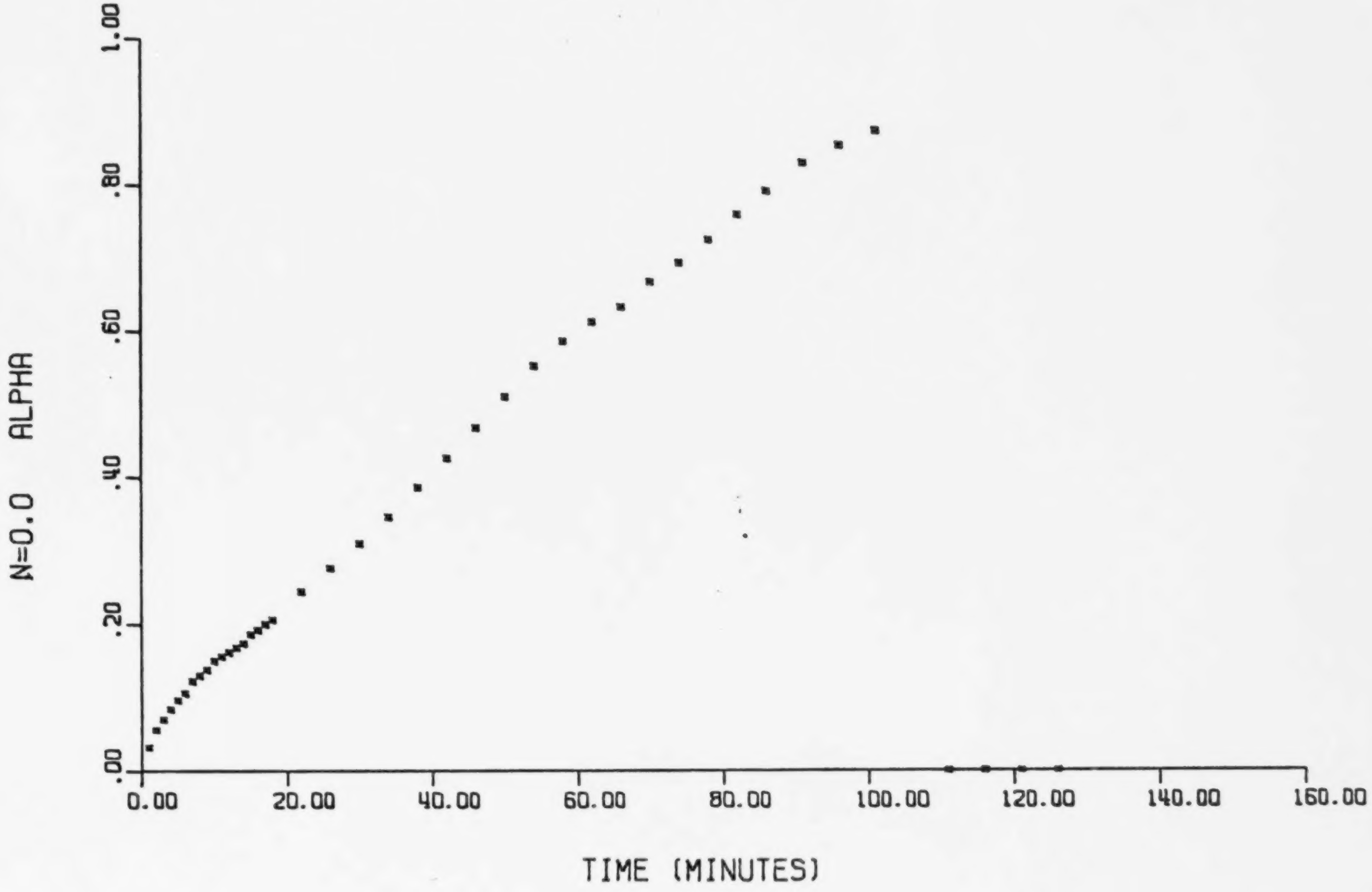
NIO 634-65-2
ISO TGA 2 TEMP = 501 DEG C



18 APR 69

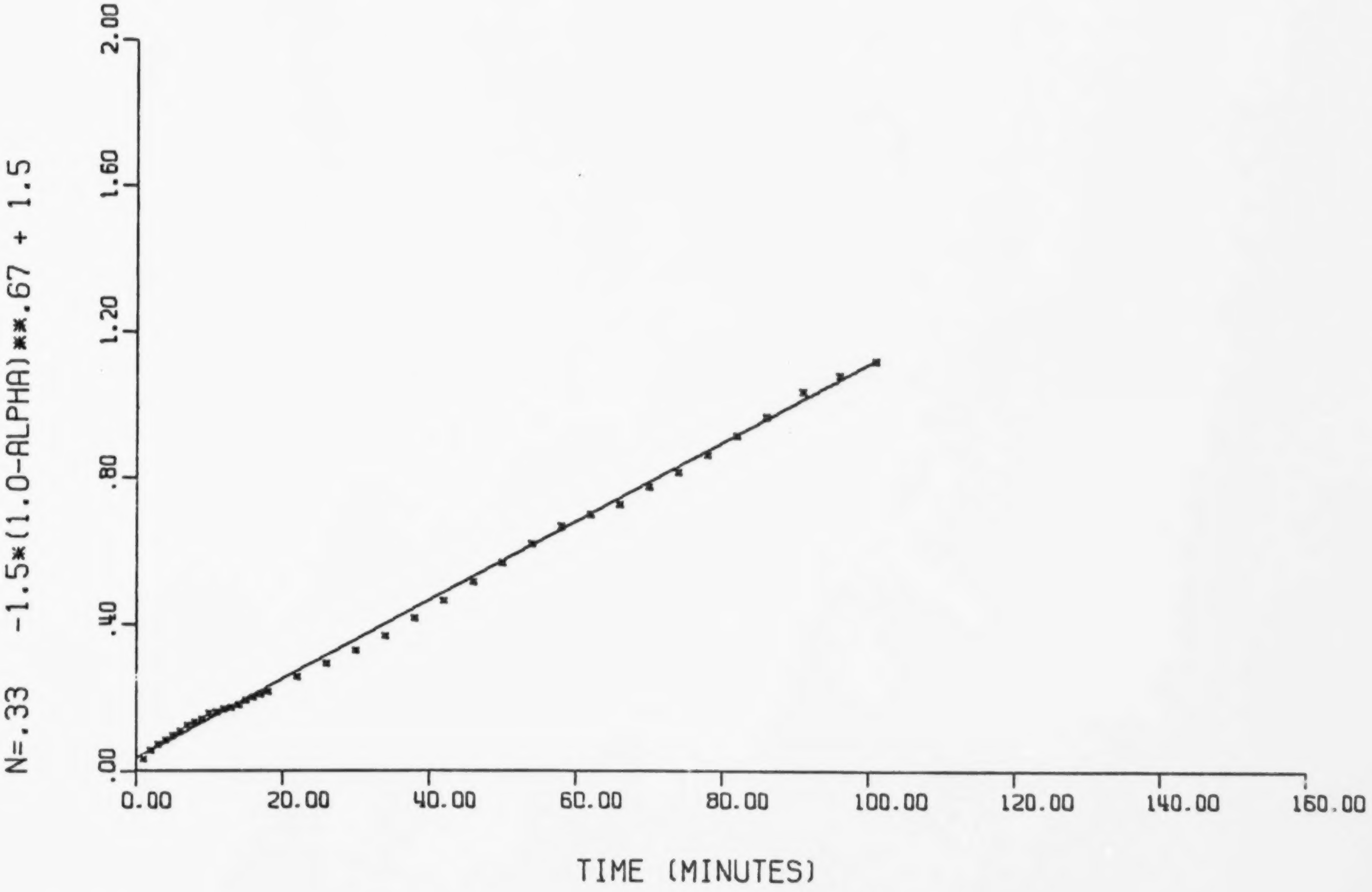
TRACOR

FE2O3 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



24 MAR 69

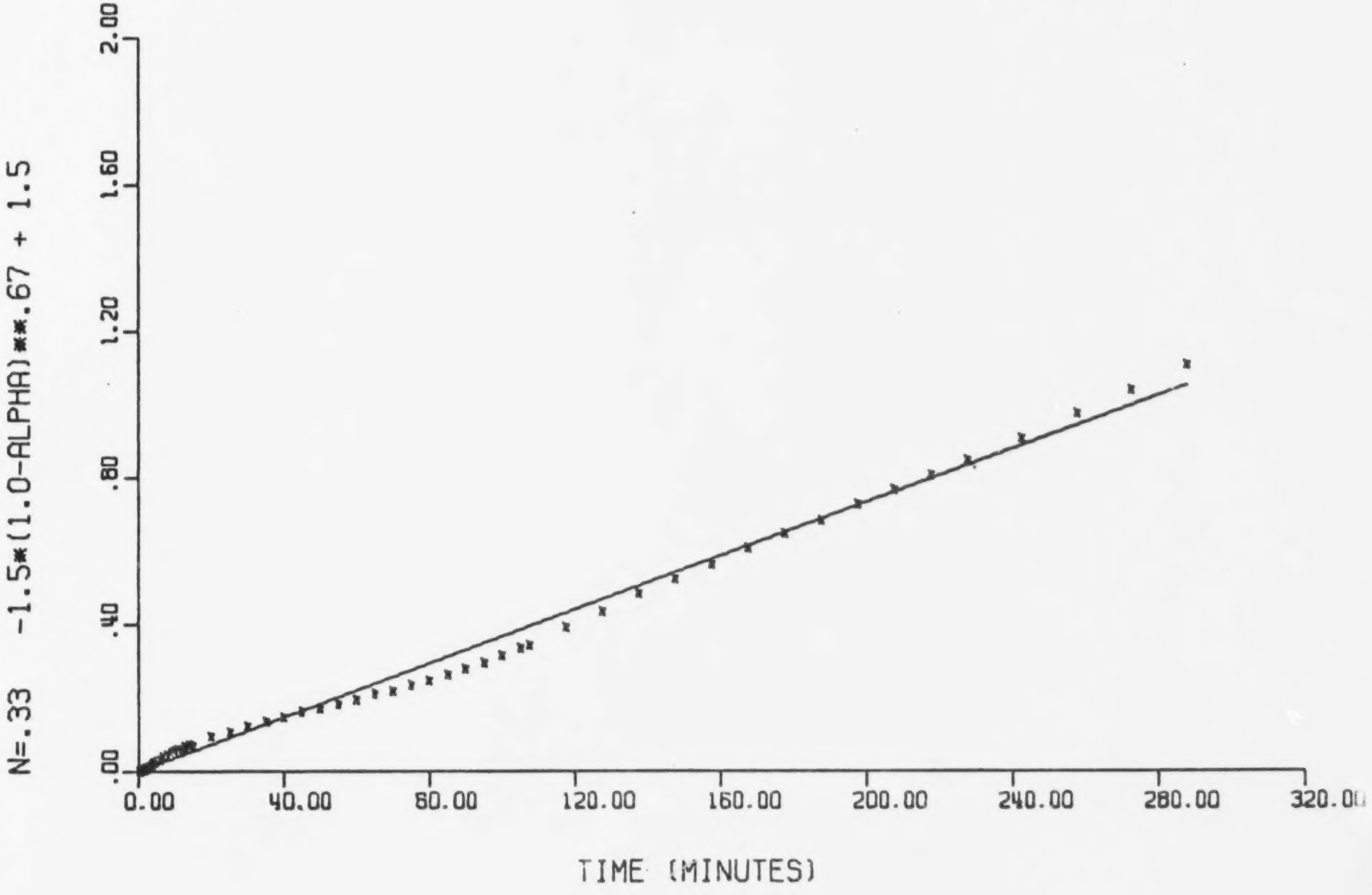
FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



14 APR 69

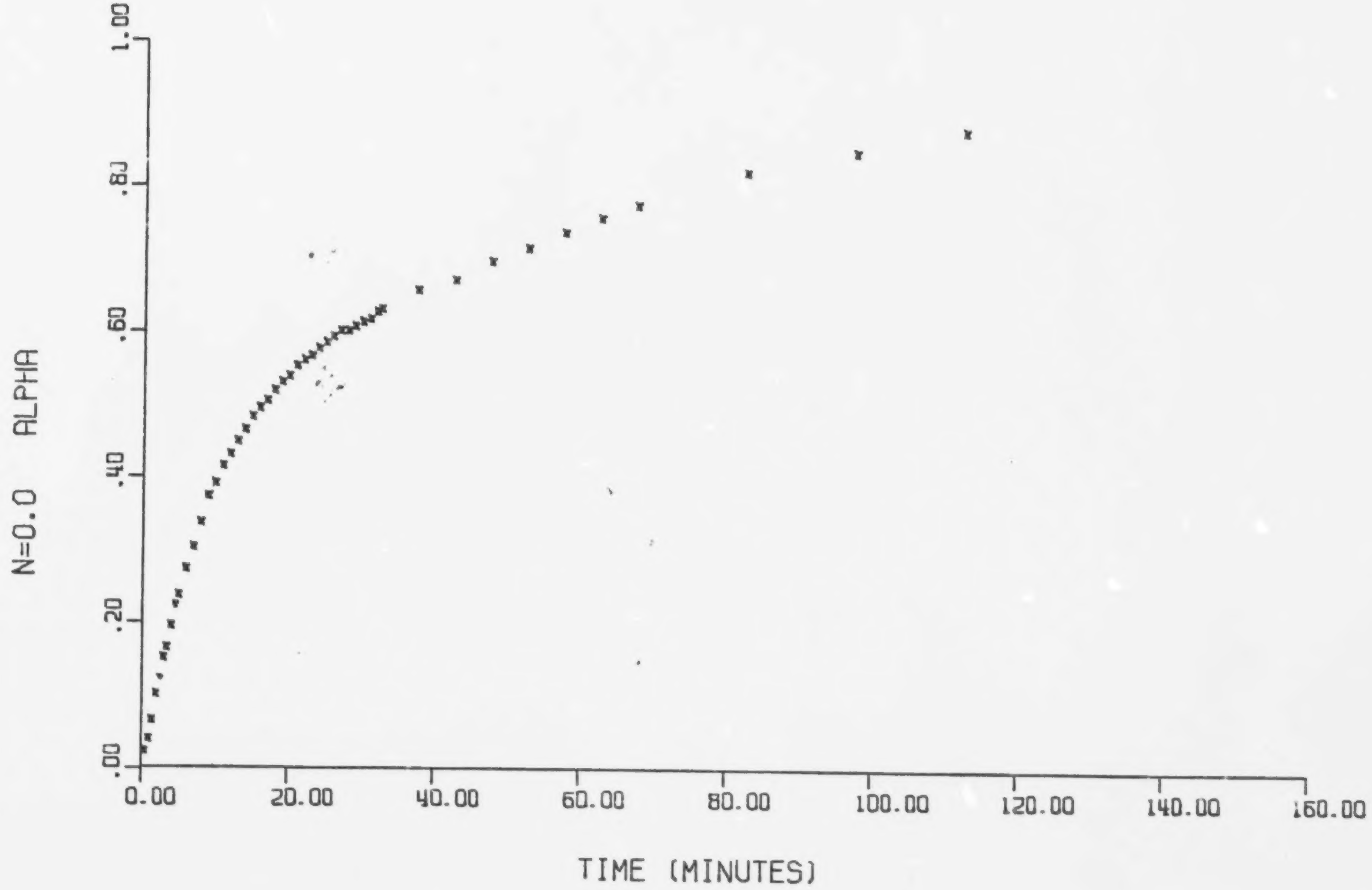
TRACOR

FE203 634-45-1
SO2 CONC = 0.120 TEMP = 400 DEG C



15 APR 69

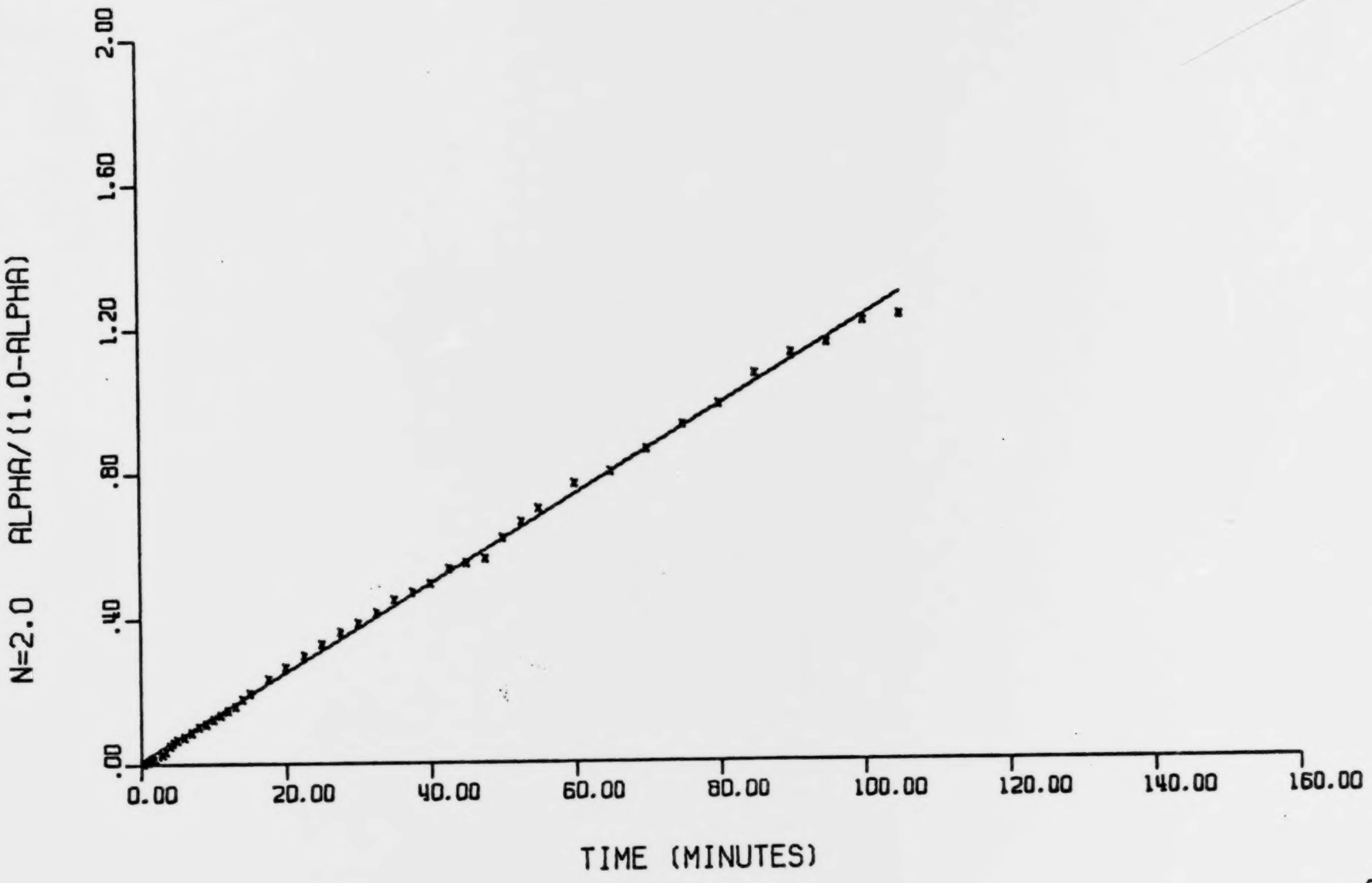
CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

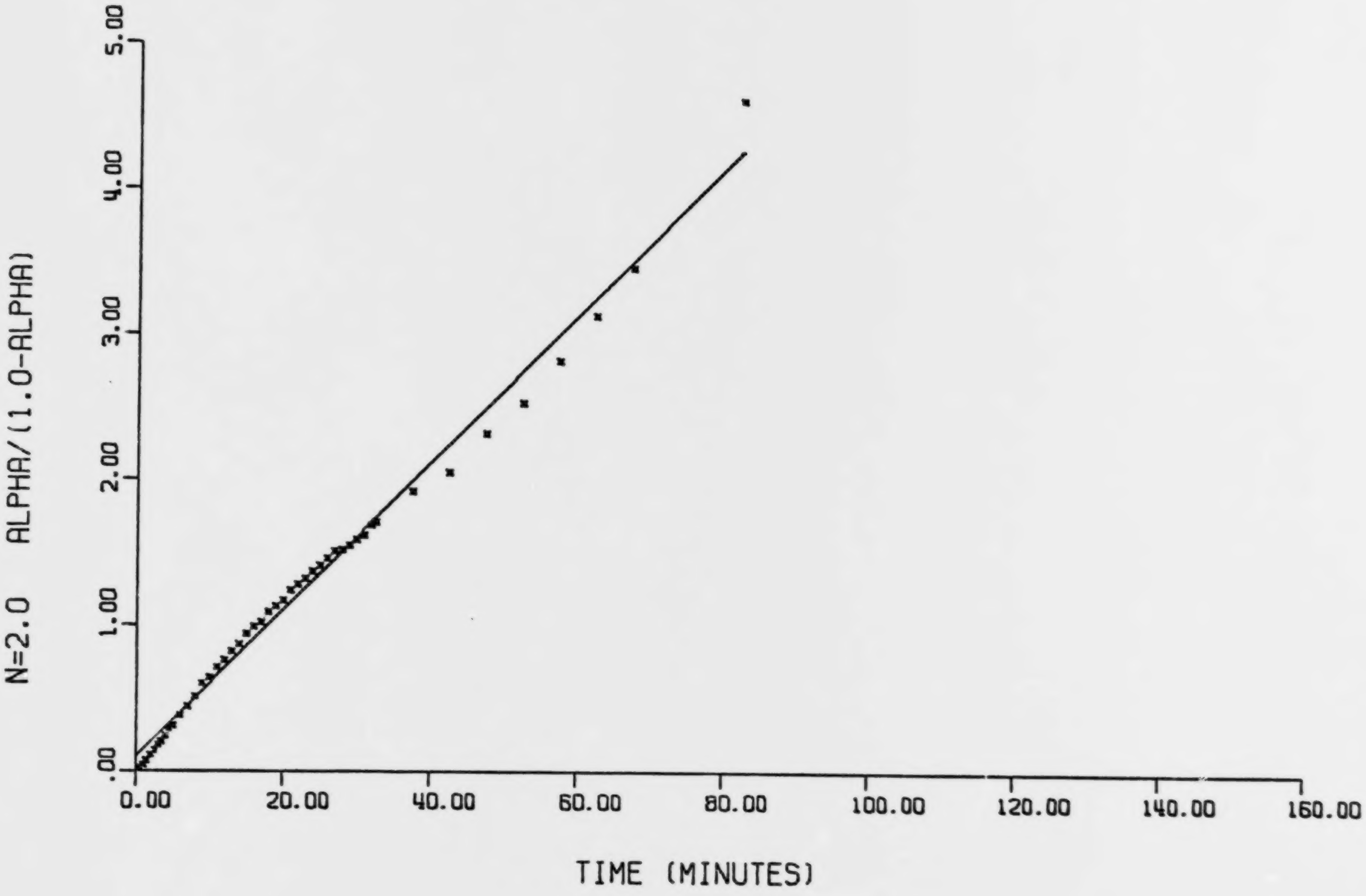
TRACOR

CEO2 634-37-1
SO2 CONC 0.127 TEMP = 194 DEG C



18 APR 69

CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



14 APR 69

APPENDIX C

FLOWCHART OF LINKED UNIT OPERATIONS PROGRAM

```
            1
-----------------------------------
   WH = WEIGHT OF SORBER HEADS
   (GM)

   WS = WEIGHT OF SORBER SHELL
   (GM)

   WV = WEIGHT OF SORBER VESSEL
   (GM)

   WD = WEIGHT OF SORBER DISTR.
   PLATE (GM)

   CLIN = COST OF SORBER LINING
   (DOLLARS)

   COSTV = COST OF SORBER VESSEL
   (DOLLARS)

   TCOSTS = TOTAL COST OF SORBER
   (DOLLARS)

   EFP = REMOVAL EFFICIENCY OF
   CYCLONE (%)

   DIACYC = DIAMETER OF CYCLONE
   (CM)

   WC = WEIGHT OF CYCLONE (GM)

   CCYC = COST OF CYCLONE
   (DOLLARS)

   VCYC = INLET VELOCITY OF
   CYCLONE (CM/SEC)

   D50 = PARTICLE SIZE WHICH
   GIVES AN EFFICIENCY OF 50%
   (MICRONS)

   DP = CYCLONE PARTICLE SIZE
   (MICRONS)
-----------------------------------
```

```
         15
----------------------------------------
   QICYC = CYCLONE INDIVIDUAL
   FLOW RATE (CC/SEC)

   TCCYC = TOTAL COST OF ALL
   CYCLONES (DOLLARS)

   DIABED = DIAMETER OF FLUIDIZED
   BED (CM)

   HBED = HEIGHT OF FLUIDIZED BED
   (CM)

   DELPS = PRESSURE DROP THRU
   SORBER (ATMOSPHERES)

   GMF = MIN. FLUID MASS VELOCITY
   (GM/SEC-CM**2)

   DBI = INITIAL BUBBLE DIAMETER
   (CM)

   DBF = FINAL BUBBLE DIAMETER
   (CM)

   EPS = MIN. FLUID VOIDAGE (NO
   UNITS)

   UMF = MIN. FLUID VELOCITY
   (CM/SEC)

   UBI = INITIAL BUBBLE VELOCITY
   (CM/SEC)

   UBF = FINAL BUBBLE VELOCITY
   (CM/SEC)

   NO = NUMBER OF HOLES IN DISTR.
   PLATE PER SQ. CM.

   WSORB = WEIGHT OF SORBENT (GM)

   DELH = GAS DISTR. PLATE
   PRESSURE DROP (CM.WATER)
----------------------------------------
```

```
             30
------------------------------------
   HVES = HEIGHT OF FLUIDIZED BED
   VESSEL (CM)

   VTP = TERMINAL VELOCITY OF
   PARTICLE (CM/SEC)

   TPDBED = TOTAL PRESSURE DROP
   IN FLUIDIZED BED (CM. WATER)

   OPRES = OUTLET PRESSURE OF
   FLUIDIZED BED (ATMOSPHERES)

   KFLG = FLAG DENOTES
   RELATIONSHIP OF UO TO VTP.

   KFLG  = 0, UO.LE..5* VTP

   KFLG  = 1, UO.GT..5* VTP

   RAT = UO/VTP (DEFINED ONLY IF
   KFLG = 1.

   IFLG = FLAG DENOTES TYPE OF
   EXIT FROM FLUBED

   IFLG = 1, NORMAL

   IFLG = 2,HEIGHT OF FLUIDIZED
   BED DID NOT CONVERGE

   IFLG = 3,REYNOLDS NO. GT.
   1000.

   IFLG = 4,LINEAR APPROXIMATION
   TO BED HEIGHT OUT OF RANGE

   IFLG = 6,INCORRECT CALCULATION
   OF TERMINAL VELOCITY

   FS = FAN SPEED (RPS)

   EFAN = OVERALL EFFICIENCY OF
   FAN (%)
------------------------------------
```

```
          46
-----------------------------------
   QIFAN = INDIVIDUAL FAN FLOW
   RATE (CC/SEC)

   DWFAN = DIAMETER OF FAN WHEEL
   (CM)

   DHPFAN = FAN DRIVER POWER
   (KCAL/SEC)

   FNCOST = FAN COST (DOLLARS)

   MOTPWR = FAN MOTOR INPUT POWER
   (KCAL/SEC)

   COSTDR = FAN DRIVER COST
   (DOLLARS)

   COSTFN = COST OF ONE FAN UNIT
   (DOLLARS)

   DRVPWR = POWER USED BY FAN
   DRIVER (KCAL/SEC)

   CSTFNS = TOTAL COST OF ALL FAN
   UNITS (DOLLARS)

   IFAN = FLAG DENOTES TYPE OF
   RETURN FROM FANCST

   IFAN = 0,NORMAL

   IFAN = 1,SUM OF INDIVIDUAL FAN
   CAPACITIES IS LESS THAN 100

   PERCENT OF CAPACITY FOR ONE
   FAN.

   TK = THICKNESS OF FLUIDIZED
   BED SHELL (CM)

   P = TOTAL INLET PRESSURE TO
   FLUIDIZED BED SYSTEM
   (ATMOSPHERES)
-----------------------------------
```

```
          61
-------------------------------------
   TC = TEMPERATURE OF FLUE GAS
   (DEG. C)

   MU = VISCOSITY OF FLUE GAS
   (GM/CM-SEC)

   RHOG = DENSITY OF FLUE GAS
   (GM/CC)

   D = DIFFUSION COEFFICIENT (SQ.
   CM/SEC)

   RHOS = DENSITY OF SOLID
   (ENG-LBS/FT**3,CGS-GM/CC)

   DPI = INPUT DIAMETER OF
   PARTICLE (ENG-IN.,CGS-CM)

   P = INPUT PRESSURE OF SYSTEM
   (ENG-PSIA,CGS-ATMOSPHERES)

   T = TEMPERATURE OF SYSTEM
   (ENG-DEG. F,CGS -DEG.C )

   RATIO = RATIO OF SUPERFICIAL
   VELOCITY TO MIN. FLUID
   VELOCITY

   (NO UNITS)

   GAMMAB = FRACTIONS OF SOLIDS
   IN BUBBLE (NO UNITS)

   ALPHA = RATIO OF VOL. OF WAKE
   TO VOL. OF BUBBLE (NO UNITS)

   CABO = OUTLET GAS
   CONCENTRATION (MOLE %)

   CABI = INLET GAS CONCENTRATION
   (MOLE %)

   KR = REACTION RATE (1/SEC)
-------------------------------------
```

```
          76
---------------------------------------
   Q = FLOW RATE OF FLUIDIZED BED
   (ENG-SCFM,CGS-CCESTP/SEC)

   CINDEX = CURRENT COST INDEX
   (NO UNITS)

   PDCYC = PRESSURE DROP OF
   CYCLONE (ENG= IN. WATER, CGS-
   CM.WATER)

   EFFCYC = EFFICIENCY OF CYCLONE
   (FRACTION)

   CYCNUM = NUMBER OF CYCLONES
   (NO UNITS)

   FANNUM = NUMBER OF FANS (NO
   UNITS)

   ITITLE = TITLE CORRESPONDING
   TO CURRENT COST INDEX

   IUNITS = TYPE OF UNITS INPUT
   WILL BE IN.

   UNITS = ENG, ENGLISH UNITS

   UNITS = CGS, CGS UNITS

   IOUT   = 0, PRINT OUT IN
   ENGLISH UNITS ONLY

   = 1, PRINT OUT IN ENGLISH AND
   CGS UNITS

   CLANG = ARRAY OF LANG FACTOR
   TO BE CHANGE

   CLANG(I,2)=1 THEN THIS IS TO
   CHANGE LANG(I)= CLANG(I,1)

   LANG = ARRAY OF BUILT IN LANG
   FACTORS
---------------------------------------
```

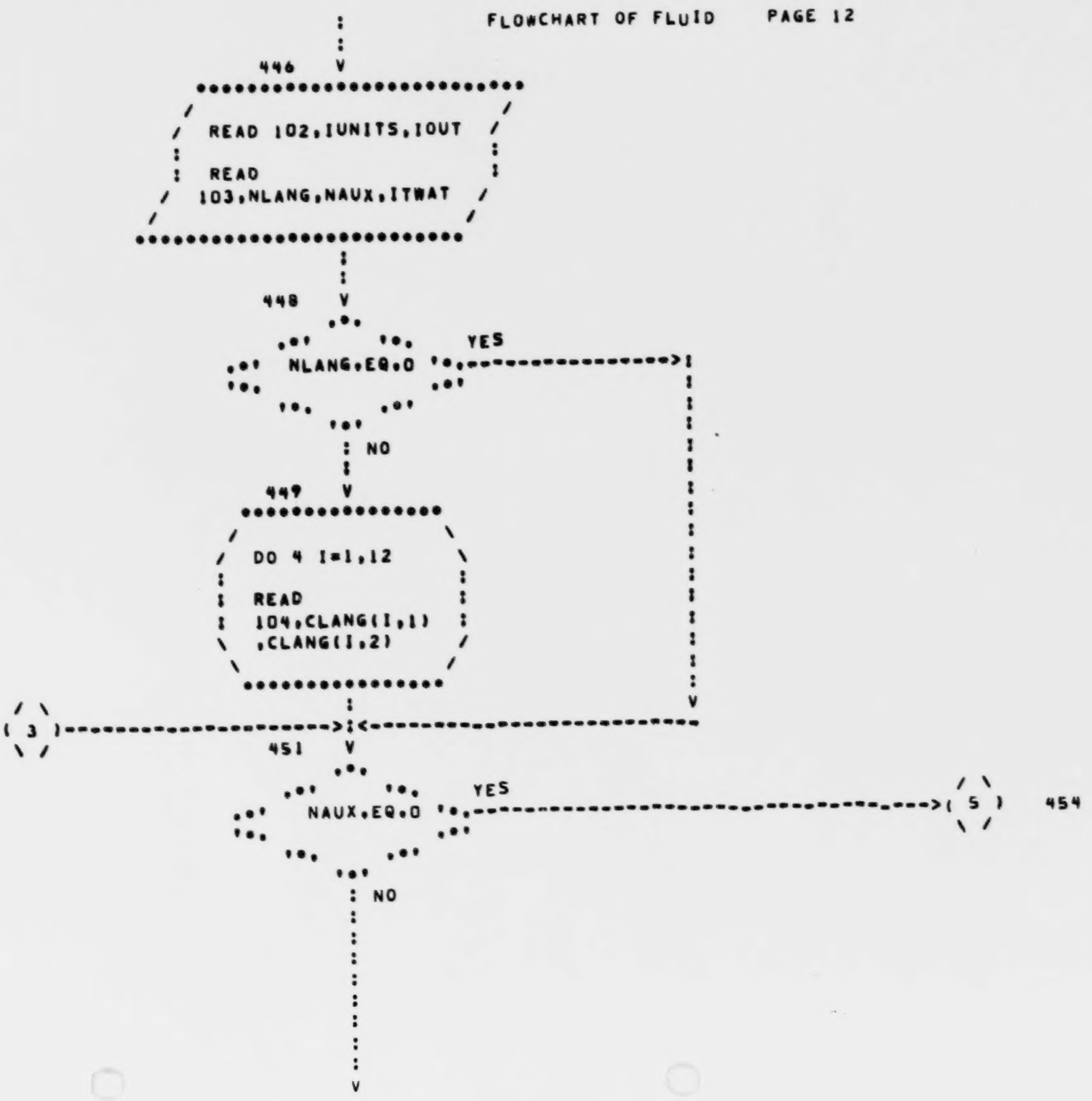
```
          91
------------------------------------
   LANG( 1)= ERECTION LABOR

   LANG( 2)= FOUNDATION AND
   PLATFORMS

   LANG( 3)= PIPING

   LANG( 4) = INSTRUMENTS

   LANG( 5) = INSULATION

   LANG( 6) = ELECTRICAL

   LANG( 7) = BUILDING

   LANG( 8) = LAND & YARD
   IMPROVEMENTS

   LANG( 9) = UTILITIES

   LANG(10) = ENGINEERING &
   CONSTRUCTION

   LANG(11) = CONTRACTOR'S FEE

   LANG(12) = CONTINGENCY

   CAUX = ARRAY OF AUXILLARY
   FACTORS TO BE CHANGED

   LAUX(I,2)=1 THEN THIS IS TO
   CHANGE AUX(I)= CAUX(D,I)

   AUX = ARRAY OF BUILT IN LANG
   FACTORS

   AUX(1)= DEPRECIATION FACTOR

   AUX(2)= UTILITIES DEPRECIATION
   FACTOR

   PE = PURCHASED EQUIPMENT COST
   (DOLLARS)
------------------------------------
```

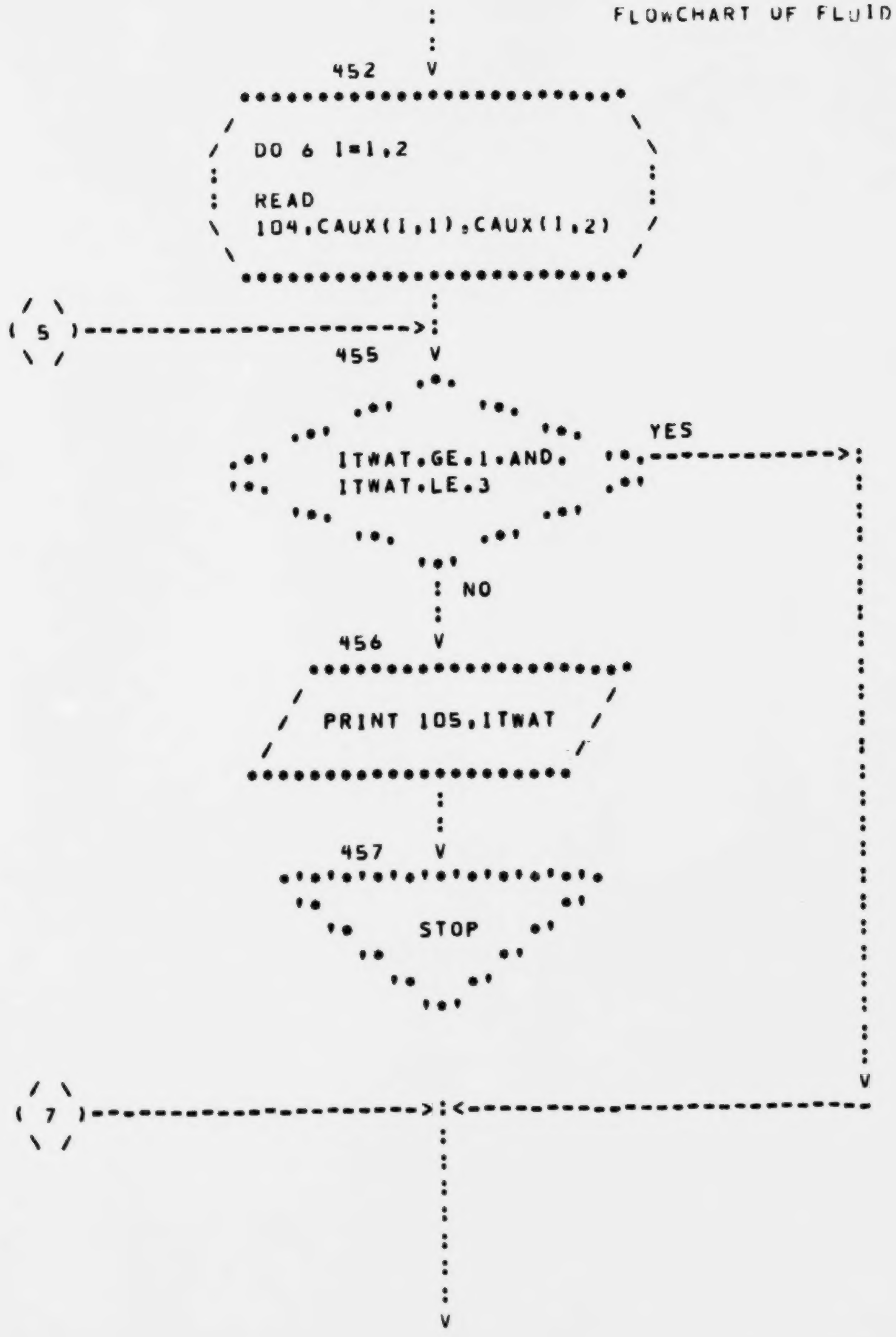
```
             109
-----------------------------------
   KCAL = POWER INPUT TO CAPITAL
   COST ROUTINES (KCAL/SEC)

   WRKNO = NUMBER OF WORKERS

   FLSUP = NO. OF FIRST LINE
   SUPERINTENDENTS

   ARASUP= NO. OF AREA
   SUPERVISORS

   ITWAT = FLAG DENOTES TYPE OF
   WATER USAGE

   =1,RAW

   =2,PROCESSED

   =3,COOLING TOWER

   OTHER1 = MISC. OPERATING
   EXPENSES (DOLLARS)

   OTHER2 = DIRECT OPER.
   EXP.(DOLLARS)

   OTHER3 = INDIRECT OPER. EXP.
   (DOLLARS)

   RMC = RAW MATERIAL & CHEMICALS
   (DOLLARS)

   PS = PACKING & SHIPPING
   (DOLLARS)

   WD = WASTE DISPOSAL (DOLLARS)

   YEAR = NO. OF YEARS OF
   OPERATION

   COAL = AMOUNT OF COAL (KGAMS)

   STMUSG = STEAM USAGE (GM/SEC)
-----------------------------------
```

```
            126
------------------------------------
   STMCDT = STEAM CREDIT (GM/SEC)

   WATUSG   WATER USAGE (CC/SEC)

   AIRUSG = AIR USAGE (CC/SEC)

   MAIN= MAINTAINCE ($)

   SUPPLY = SUPPLIES ($)

   DL = DIRECT LABOR ($)

   SUP = SUPERVISORS ($)

   STEAM = STEAM ($)

   ELEC = ELECTRICITY ($)

   AIR = AIR ($)

   WATER = WATER ($)

   UTIL2 = TOTAL UTILITIES ($)
   FROM OPERATING COST

   TDC = TOTAL DIRECT COST ($)

   PAYROL = PAYROLL ($)

   PO = PLANT OVERHEAD ($)

   TIC = TOTAL INDIRECT COST ($)

   DEP = DEPRECIATION ($)

   TAXES = TAXES ($)

   INS = INSURANCE ($)

   TFC = TOTAL FIXED COST ($)

   TOC = TOTAL OPERATING COST ($)
------------------------------------
```

```
        147
------------------------------------
  COSTD=$/TON OF COAL

  TON = TONS OF COAL

  COSTM = MIL-KWH ($)

  EL = ERECTION LABOR ($)

  FP = FOUNDATION AND PLATFORMS
  ($)

  PIPE = PIPING ($)

  INST = INSTRUMENTS ($)

  INSUL= INSULATION ($)

  ELEC = ELECTRICITY ($)

  BUILD = BUILDING ($)

  LYI = LAND & YARD IMPROVEMENTS
  ($)

  UTILI = UTILITIES OF CAPITAL
  COST ($)

  EC = ENGINEERING &
  CONSTRUCTION ($)

  CF = CONTRACTORS FEE ($)

  CONT = CONTINGECIES ($)

  PPC = PHYSICAL PLANT COST ($)

  DPC = DIRECT PLANT COST ($)

  FCC = FIXED CAPITAL COST ($)

  WC = WORKING CAPITAL ($)

  TI = TOTAL INVESTMENT ($)
------------------------------------
```

```
             167
 -----------------------------------
    CR = CAPITAL REQUIREMENTS ($)

    NLANG = FLAG DENOTES WHETHER
    CHANGE LANG FACTORS OR NOT

    =0, DO NOT CHANGE

    =1, CHANGE  IF 1, THEN READ IN
    12.

    NAUX = FLAG DENOTES CHANGE
    AUXILLARY FACTOR OR NOT

    =0, DO NOT CHANGE

    =1, CHANGE  IF 1, THEN READ IN
    2.

    FANCAP = FRACTION OF TOTAL FAN
    CAPACITY FOR EACH UNIT
 -----------------------------------


             443
     ..........................
    /                          \
   /  CALL DATE(MON,IDAY,IYEAR)  \
   \                             /
    \                          /
     ..........................
                 :
                 :
             444 V
       ......................
       .                    .
       .  IMONTH=MONTH(MON) .
       .                    .
       ......................
  /   \          :
 ( 802 )-------->:
  \   /          :
                 :
                 :
                 :
                 :
                 V
```

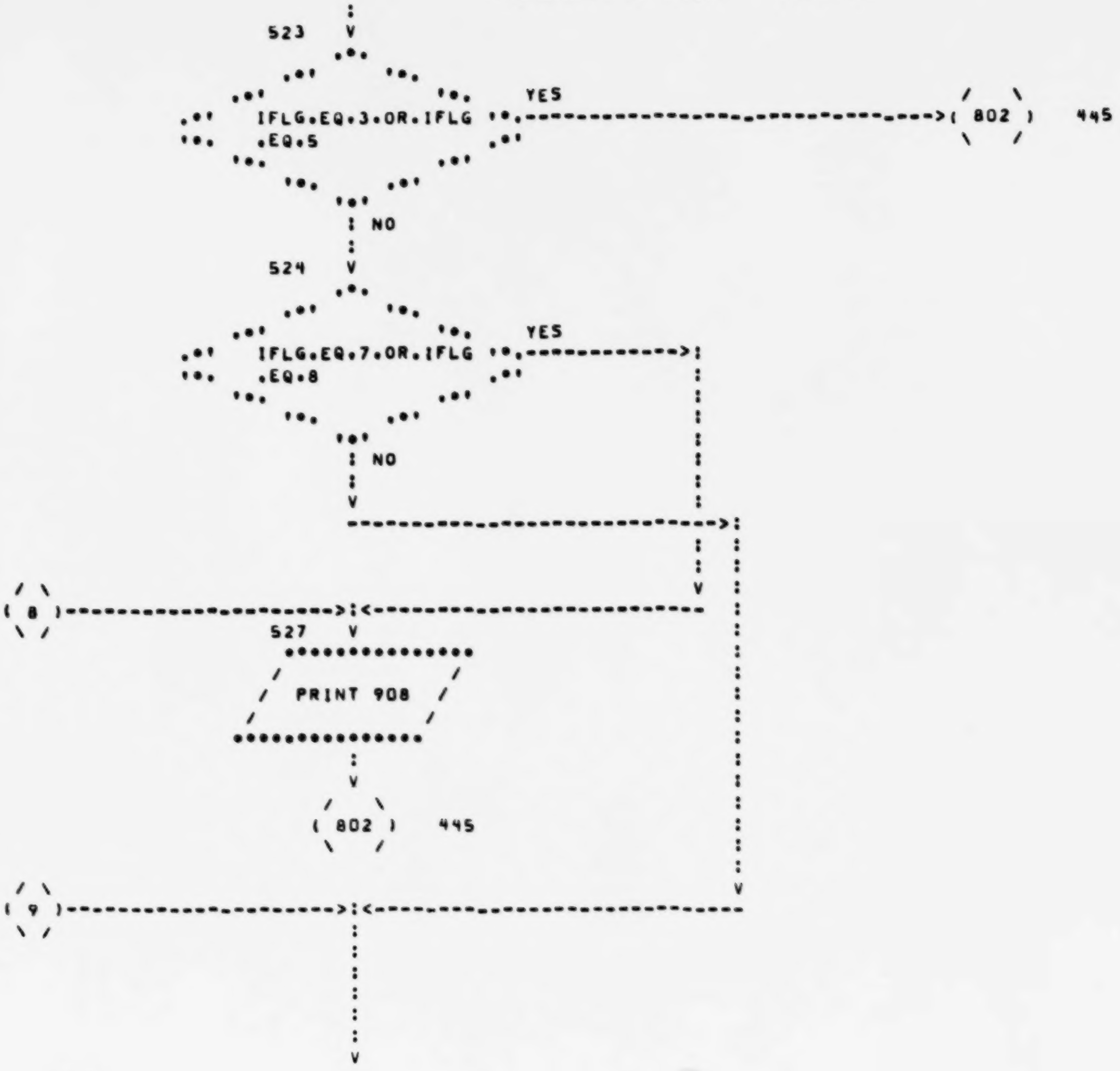

446
READ 102,IUNITS,IOUT
READ
103,NLANG,NAUX,ITWAT
448
NLANG.EQ.0
YES
NO
449
DO 4 I=1,12
READ
104,CLANG(I,1)
,CLANG(I,2)
3
451
NAUX.EQ.0
YES
5
454
NO


452
DO 6 I=1,2
READ
104,CAUX(I,1),CAUX(I,2)
5
455
ITWAT.GE.1.AND.
ITWAT.LE.3
YES
NO
456
PRINT 105,ITWAT
457
STOP
7

```
                  :
                  :
             459  V
     *******************************
    /                             /
   /  READ                       /
   :  100,RHOS,DPI,P,T,RATIO,     :
   :  GAMMAB,ALPHA,CABO,CABI,     :
   :  KR,Q,CINDEX,                :
   :  PDCYC,EFFCYC,CYCNUM,        :
   :  FANNUM,FANCAP               :
   :                              :
   :  READ                        :
   :  106,KCAL,WRKNO,FLSUP,       :
   :  ARASUP,OTHER1,OTHER2,       :
   :  OTHER3,RMC,                 :
   :  PS,WSD,YEAR,COAL,SIMUSG,    :
   :  STMCDT,WATUSG,AIRUSG        :
   :                              :
   :  READ 100,CASE               :
   :                              :
   :  READ 907,CAT,PROC           :
   :                              :
  /  READ 101,ITITLE             /
 /                             /
*******************************
                  :
                  :
            466   V
                 .*.
             .*'     '*.
         .*'             '*.      YES
     .*'    IUNITS.EQ.3HENG    '*.---------------------------------->( 1 )   494
     '*.                       .*'                                   \ /
         '*.               .*'
             '*.       .*'
                 '*'
                  : NO
                  :
            467   V
          *****************
          *               *
          *  KCALC=KCAL   *
          *               *
          *  COALC=COAL   *
          *               *
          *****************
                  :
                  :
                  :
                  v
                  :
                  :
           469    V
**********************************
*                                *
*  STMUSC=STMUSG                 *
*                                *
*  STMCDC=STMCDT                 *
*                                *
*  WATUSC=WATUSG                 *
*                                *
*  AIRUSC=AIRUSG                 *
*                                *
*  KCALE=KCAL*2.39E-4            *
*                                *
*  COALE=COAL*001102             *
*                                *
*  STMUSE=STMUSG*002205*3600.0   *
*                                *
*  STMCDE=STMCDT*002205*3600.0   *
*                                *
*  WATUSE=WATUSG*0002642*3600.0  *
*                                *
*  AIRUSE=AIRUSG*00003531*3600.0 *
*                                *
*  RHOSC=RHOS                    *
*                                *
*  DPIC=DPI                      *
*                                *
*  PC=P                          *
*                                *
*  TC=T                          *
*                                *
*  PDCYCC=PDCYC                  *
*                                *
*  QAC=(T+273.1)*Q/(273.1*PC)    *
*                                *
*  QSC=Q                         *
*                                *
*  RHOSE=62.4*RHOS               *
*                                *
*  DPIE=3937*DPI                 *
*                                *
*  PE=14.*P                      *
*                                *
*  TE=(T*9./5.)+32.0             *
*                                *
**********************************
                  :
                  :
                  V
```

```
                           :
                           :
                     490   V
             ****************************
             *                          *
             *  PDCYCE=3937*PDCYC       *
             *                          *
             *  QSE=Q/472.*289./273.16  *
             *                          *
             *  QAE=QAC/472.0           *
             *                          *
             ****************************
                           :
                           V
                          / \
                         ( 2 )   521
                          \ /

 / \
( 1 )--------------------->:
 \ /                 495   V
         *************************************
         *                                   *
         *  KCALE=KCAL                       *
         *                                   *
         *  COALE=COAL                       *
         *                                   *
         *  STMUSE=STMUSG                    *
         *                                   *
         *  STMCDE=STMCDT                    *
         *                                   *
         *  WATUSE=WATUSG                    *
         *                                   *
         *  AIRUSE=AIRUSG                    *
         *                                   *
         *  KCALC=KCAL/2.39E-4               *
         *                                   *
         *  COALC=COAL*907.1848              *
         *                                   *
         *  STMUSC=STMUSG/(002205*3600.)     *
         *                                   *
         *  STMCDC=STMCDT/(002205*3600.)     *
         *                                   *
         *  WATUSC=WATUSG/(0002642*3600.)    *
         *                                   *
         *  AIRUSC=AIRUSG/(00003531*3600.)   *
         *                                   *
         *************************************
                           :
                           :
                           V
```

```
                    :
                    :
              507   V
 ********************************
 *                              *
 *  RHOSE=RHOS                  *
 *                              *
 *  DPIE=DPI                    *
 *                              *
 *  PE=P                        *
 *                              *
 *  TE=T                        *
 *                              *
 *  PDCYCE=PDCYC                *
 *                              *
 *  RHOSC=01602*RHOS            *
 *                              *
 *  DPIC=2.5*DPI                *
 *                              *
 *  PC=P/14.7                   *
 *                              *
 *  TC=(T-32.)*5./9.0           *
 *                              *
 *  PDCYCC=PDCYC*2.54           *
 *                              *
 *  QSE=Q                       *
 *                              *
 *  QAE=Q*(TC+273.1)/(289.*PC)  *
 *                              *
 *  QAC=QAE*472.0               *
 *                              *
 *  QSC=Q*472.*273.1/289.0      *
 *                              *
 ********************************
  / \               :
 ( 2 )------------------>:
  \ /         522   V
  ******************************
 /                              \
/  CALL FLUBED(RHOSC,DPIC,PC,TC, \
:  RATIO,GAMMAB,ALPHA,CABO,CABI, :
\  KR,QAC)                       /
 \                              /
  ******************************
                    :
                    :
                    :
                    :
                    :
                    :
                    V
```


523
IFLG.EQ.3.OR.IFLG .EQ.5
YES
802
445
NO
524
IFLG.EQ.7.OR.IFLG .EQ.8
YES
NO
8
527
PRINT 908
802
445
9

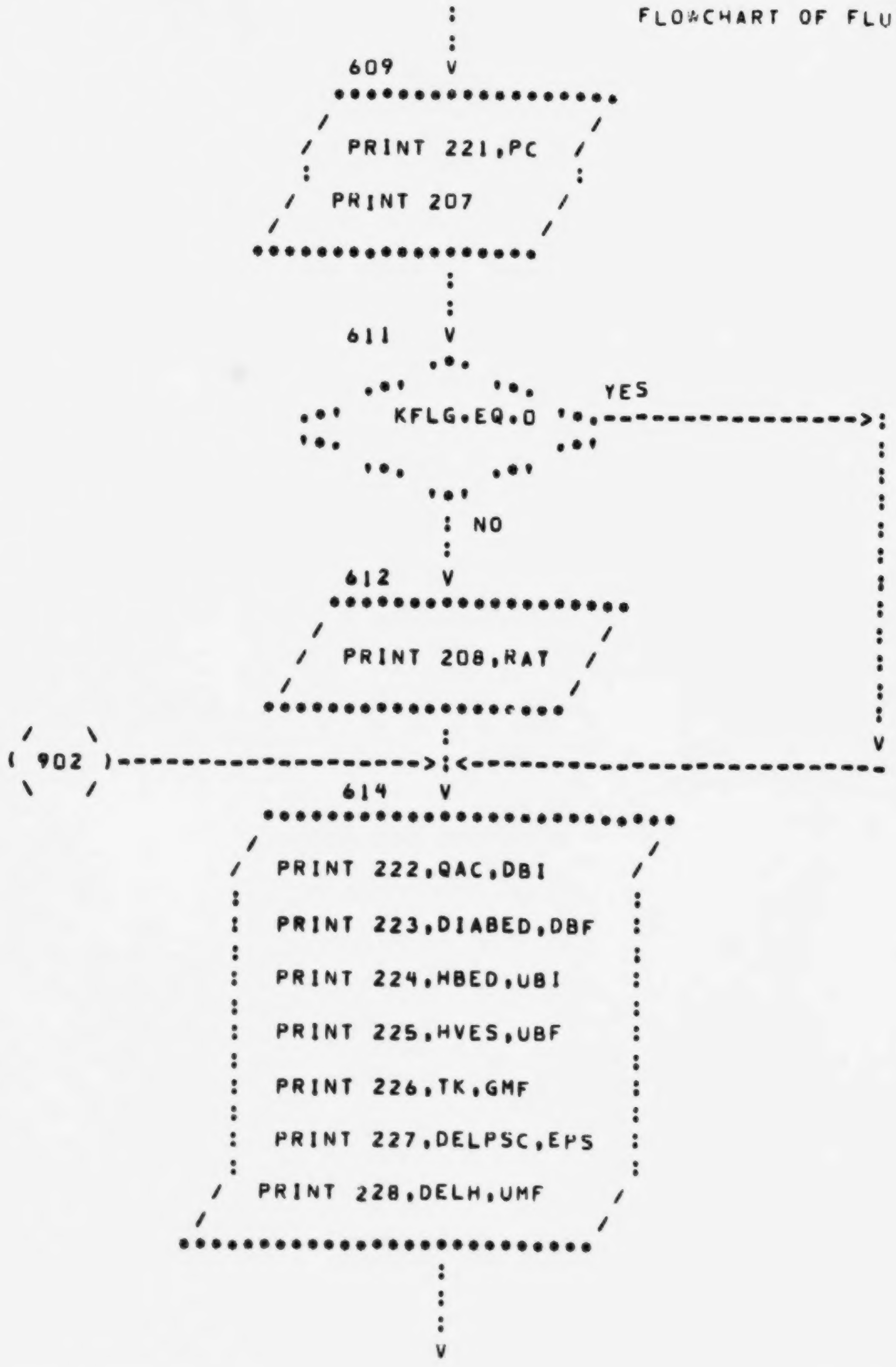
```
                         :
                         :
                  531    V
         ******************************
        /                              \
       /  CALL SORBER(CINDEX,DIABED,HVES \
       :  ,TK)                           :
       :                                 :
       :  CALL CYCLON(PDCYCC,QAC,RHOG,   :
       \  CINDEX,RHOSC,MU,EFFCYC,CYCNUM) /
        \                              /
         ******************************
                         :
                         :
                  533    V
            ***********************
            *                     *
            *  DPFAN=PDCYCC+TPQBED *
            *                     *
            ***********************
                         :
                         :
                  534    V
         *****************************
        /                             \
       /  CALL FANCST(QAC,DPFAN,RHOG,  \
       \  FANNUM,FANCAP,CINDEX,ITITLE) /
        \                             /
         *****************************
                         :
                         :
                  535    V
           **************************
           *                        *
           *  PEC=TCOSTS+TCCYC+CSTFNS *
           *                        *
           **************************
                         :
                         :
                  536    V
           **************************
          /                          \
         /  CALL CAPTAL(CLANG,CAUX,PEC, \
         \  KCALC,MW)                   /
          \                          /
           **************************
                         :
                         :
                         :
                         :
                         V
```

```
                 :
                 :
         537     V
 *******************************
 /                              \
/ CALL OPER(WRKNO,FLSUP,ARASUP,  \
: ITWAT,OTHER1,OTHER2,OTHER3,RMC :
: ,PS,WSD,YEAR,COALC,STMUSC,     :
\ STMCDC,DRVPWR,WATUSC,AIRUSC)   /
 \                              /
 *******************************
                 :
                 :
         539     V
   *************************
   *                       *
   * DIACYE=DIACYC*03281   *
   *                       *
   * WCE=WC*002205         *
   *                       *
   * VCYCE=VCYC*03281      *
   *                       *
   * QICYCE=QICYC/472.0    *
   *                       *
   * WSE=002205*WS         *
   *                       *
   * WHE=002205*WH         *
   *                       *
   * WDE=002205*WD         *
   *                       *
   * WVE=002205*WV         *
   *                       *
   * TKE=TK*3937           *
   *                       *
   * DIABEE=DIABED*03281   *
   *                       *
   * HBEDE=HBED*03281      *
   *                       *
   * DELPSE=DELPS*33.*12.0 *
   *                       *
   * DELPSC=DELPS*33.*30.48*
   *                       *
   * GMFE=GMF*2.048*3600.0 *
   *                       *
   * DBIE=DBI*03281        *
   *                       *
   *************************
                 :
                 :
                 :
                 V
```

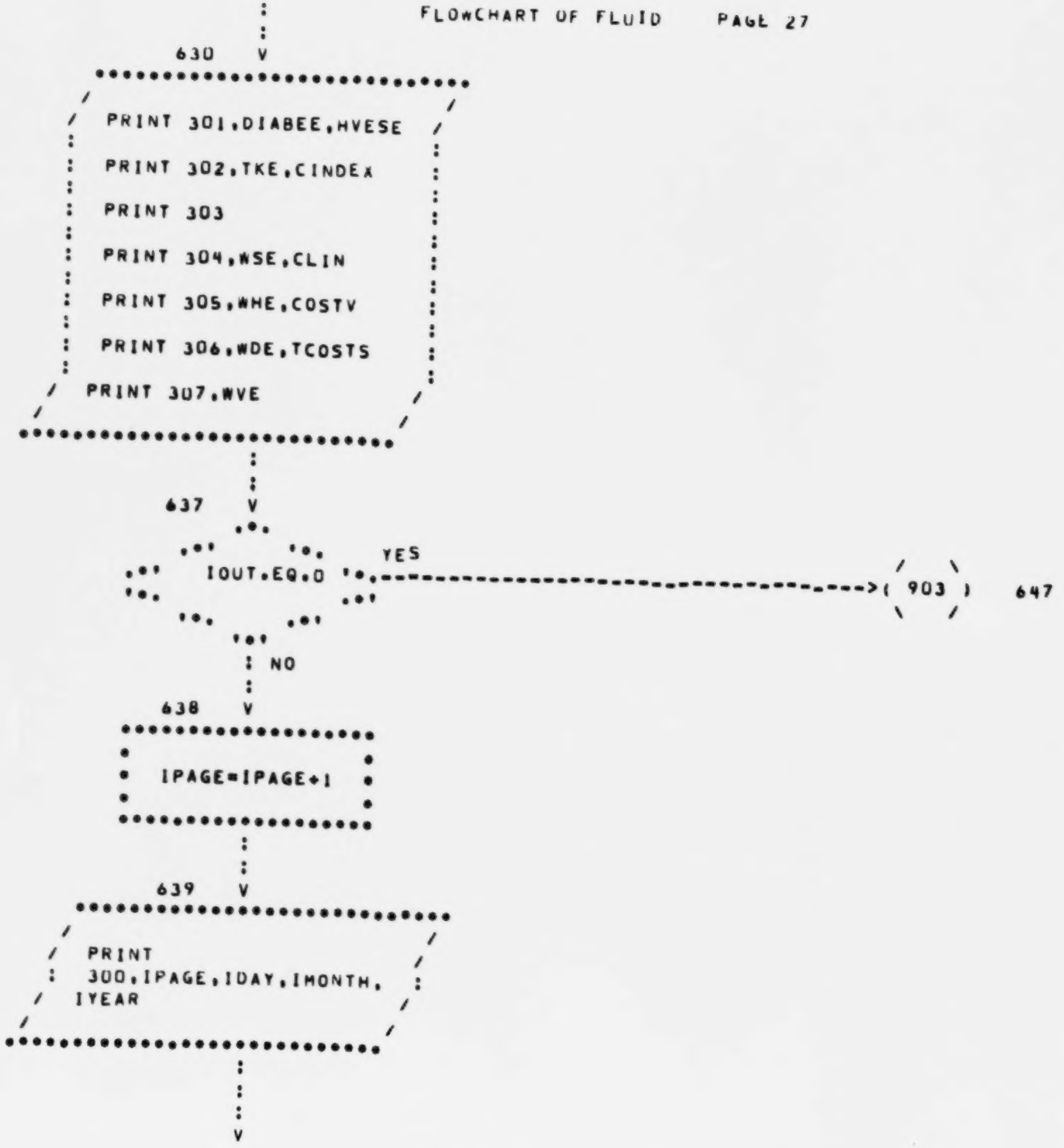
```
                    :
                    :
           554      V
      ****************************
      *                          *
      *  DBFE=DBF*03281          *
      *                          *
      *  UMFE=UMF*03281          *
      *                          *
      *  UBIE=UBI*03281          *
      *                          *
      *  UBFE=UBF*03281          *
      *                          *
      *  NOE=NO*1./155           *
      *                          *
      *  WSORBE=WSORB*002205     *
      *                          *
      *  DELHE=DELH*3937         *
      *                          *
      *  HVESE=HVES*03281        *
      *                          *
      *  VTPE=VTP*03281          *
      *                          *
      *  TPDBEE=TPDBED*3937      *
      *                          *
      *  OPRESE=OPRES*14.7       *
      *                          *
      *  QSEM=QSE/1.0E+6         *
      *                          *
      *  RHOGE=RHOG*62.43        *
      *                          *
      *  MUE=MU*30.4/454.0       *
      *                          *
      *  TKCYCE=TKCYC*3937       *
      *                          *
      *  FSE=FS*60.0             *
      *                          *
      *  DPFANE=DPFAN*3937       *
      *                          *
      *  QIFANE=QIFAN/472.0      *
      *                          *
      *  DWFANE=DWFAN*3937       *
      *                          *
      *  DHPFAE=DHPFAN*60./10.68 *
      *                          *
      *  MOTPWE=MOTPWR*60./10.68 *
      *                          *
      ****************************
                    :
                    :
                    V
```

```
                 :
                 :
          575    V
     ******************************
     *                            *
     *  DRVPWE=DRVPWR*60./14.34   *
     *                            *
     *  IPAGE=1                   *
     *                            *
     ******************************
                 :
                 :
          577    V
      ******************************
      /                           /
     /  PRINT                    /
     :  200,IPAGE,IDAY,IMONTH,   :
     :  IYEAR                    :
     :                           :
     :  PRINT 201,QSE,RHOSE      :
     :                           :
     :  PRINT 202,DPIE,CABI      :
     :                           :
     :  PRINT 203,KR,CABO        :
     :                           :
     :  PRINT 204,RATIO,ALPHA    :
     :                           :
     :  PRINT 205,TE,GAMMAB      :
     :                           :
     :  PRINT 206,PE             :
     :                           :
    /  PRINT 207                /
   /                           /
   ******************************
                 :
                 :
          585    V
                .*.
             .*'   '*.      YES
         .*'  KFLG.EQ.0 '*.------------------------------->( 900 )   587
         '*.             .*'                               \     /
             '*.     .*'
                '*'
                 : NO
                 :
                 :
                 :
                 :
                 :
                 V
```

```
                           :
                           :
                     586   V
                    ...................
                   /                 /
                  /  PRINT 208,RAT  /
                 /                 /
                ...................
                           :
 /   \                     :
( 900 )------------------->:
 \   /               588   V
                ...........................
               /                         /
              /  PRINT 209,QAE,DBIE     /
              :                         :
              :  PRINT 210,DIABEE,DBFE  :
              :                         :
              :  PRINT 211,HBEDE,WBIE   :
              :                         :
              :  PRINT 212,HVESE,UBFE   :
              :                         :
              :  PRINT 213,TKE   ,GMFE  :
              :                         :
              :  PRINT 214,DELPSE,EPS   :
              :                         :
              :  PRINT 215,DELHE,UMFE   :
              :                         :
              :  PRINT 216,TPDBEE,NOE   :
              :                         :
             /  PRINT 217,OPRESE,VTPE /
            /                         /
           ...........................
                           :
                           :
                     597   V
                .......................
                .                     .
                .  SPVELE=RATIO*UMFE  .
                .                     .
                .......................
                           :
                           :
                     598   V
               .............................
              /                           /
             /  PRINT 231,WSORBE,SPVELE  /
            /                           /
           .............................
                           :
                           :
                           V
                 :
                 :
           599   V
     ****************************
    /                           /
   /  PRINT 233,GAMMAC,DELTA   /
   :                          :
  /  PRINT 234,GAMMAE         /
 /                           /
****************************
                 :
                 :
           601   V
                .*.
            .*'     '*.     YES
        .*'   IOUT.EQ.0 '*.-------------------------------------->( 901 )   627
        '*.                .*'                                     \     /
            '*.     .*'
                '*'
                 : NO
                 :
           602   V
        *******************
        *                 *
        *  IPAGE=IPAGE+1  *
        *                 *
        *******************
                 :
                 :
           603   V
     ****************************
    /                           /
   /  PRINT                    /
   :  200,IPAGE,IDAY,IMONTH,  :
   :  IYEAR                   :
   :                          :
   :  PRINT 218,QSC,RHOSC     :
   :                          :
   :  PRINT 219,DPIC,CABI     :
   :                          :
   :  PRINT 203,KR,CABO       :
   :                          :
   :  PRINT 204,RATIO,ALPHA   :
   :                          :
  /  PRINT 220,TC,GAMMAB      /
 /                           /
****************************
                 :
                 :
                 :
                 V
```

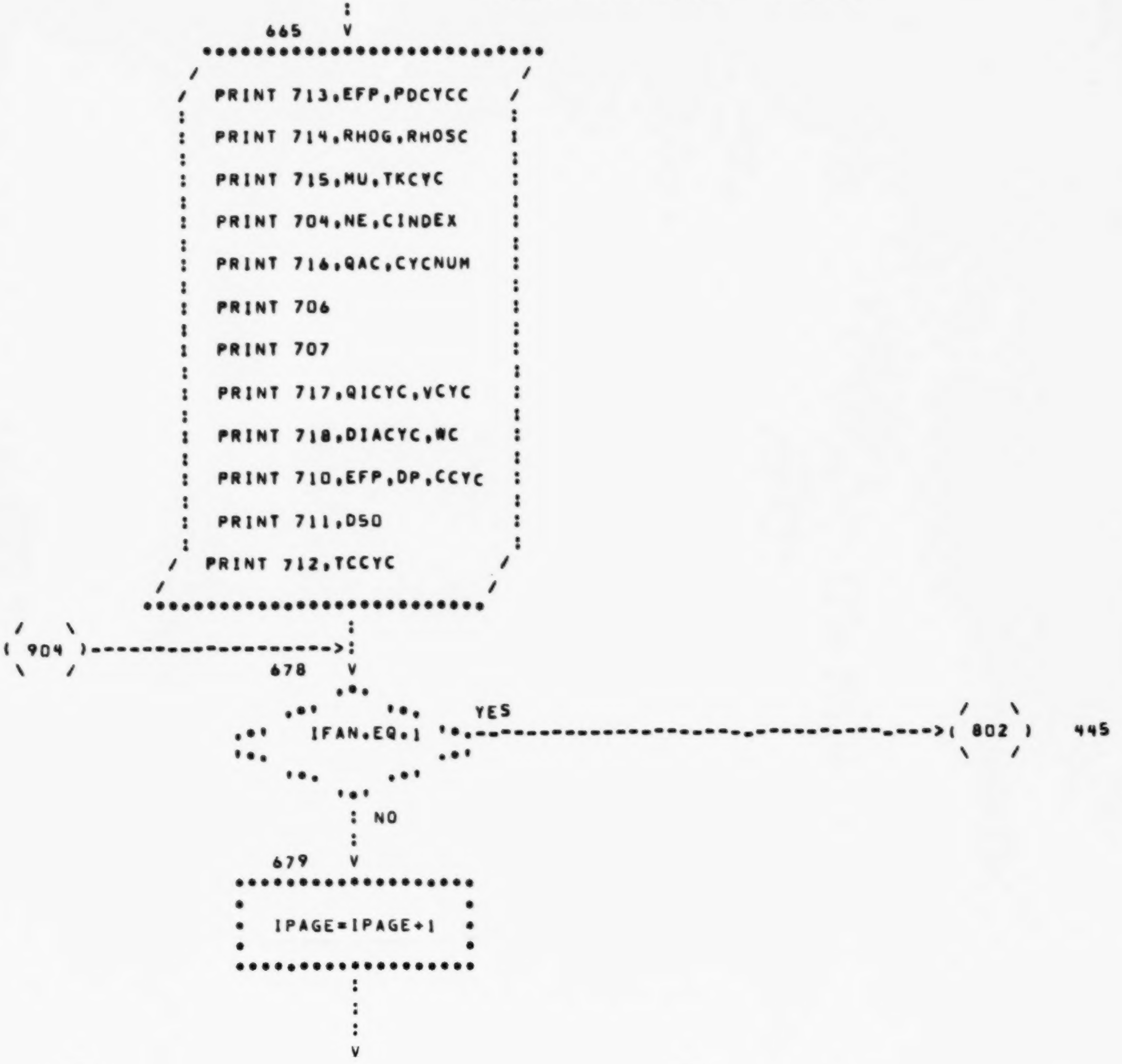

609
PRINT 221,PC
PRINT 207
611
KFLG.EQ.0
YES
NO
612
PRINT 208,RAT
902
614
PRINT 222,QAC,DBI
PRINT 223,DIABED,DBF
PRINT 224,HBED,UBI
PRINT 225,HVES,UBF
PRINT 226,TK,GMF
PRINT 227,DELPSC,EPS
PRINT 228,DELH,UMF

```
                           :
                           :
                     621   V
                 ••••••••••••••••••••••••••
                 /                       /
                /  PRINT 229,TPDBED,NO  /
                :                       :
               /  PRINT 230,OPRES,VTP  /
              /                       /
            ••••••••••••••••••••••••••
                           :
                           :
                     623   V
                ••••••••••••••••••••••
                •                    •
                •  SPVELC=RATIO*UMF  •
                •                    •
                ••••••••••••••••••••••
                           :
                           :
                     624   V
               •••••••••••••••••••••••••••••
              /                           /
             /  PRINT 232,WSORB,SPVELC   /
             :                           :
             :  PRINT 233,GAMMAC,DELTA   :
             :                           :
            /  PRINT 234,GAMMAE         /
           /                           /
          •••••••••••••••••••••••••••••
                           :
  /   \                    :
( 901 )------------------->:
  \   /              628   V
                  ••••••••••••••••••••
                  •                  •
                  •  IPAGE=IPAGE+1   •
                  •                  •
                  ••••••••••••••••••••
                           :
                           :
                     629   V
               •••••••••••••••••••••••••••••
               /                          /
              /  PRINT                   /
              :  300,IPAGE,IDAY,IMONTH,  :
             /  IYEAR                   /
            /                          /
           •••••••••••••••••••••••••••••
                           :
                           :
                           V
```


630
PRINT 301,DIABEE,HVESE
PRINT 302,TKE,CINDEX
PRINT 303
PRINT 304,WSE,CLIN
PRINT 305,WHE,COSTV
PRINT 306,WDE,TCOSTS
PRINT 307,WVE
637
IOUT.EQ.0
YES
903
647
NO
638
IPAGE=IPAGE+1
639
PRINT
300,IPAGE,IDAY,IMONTH,
IYEAR

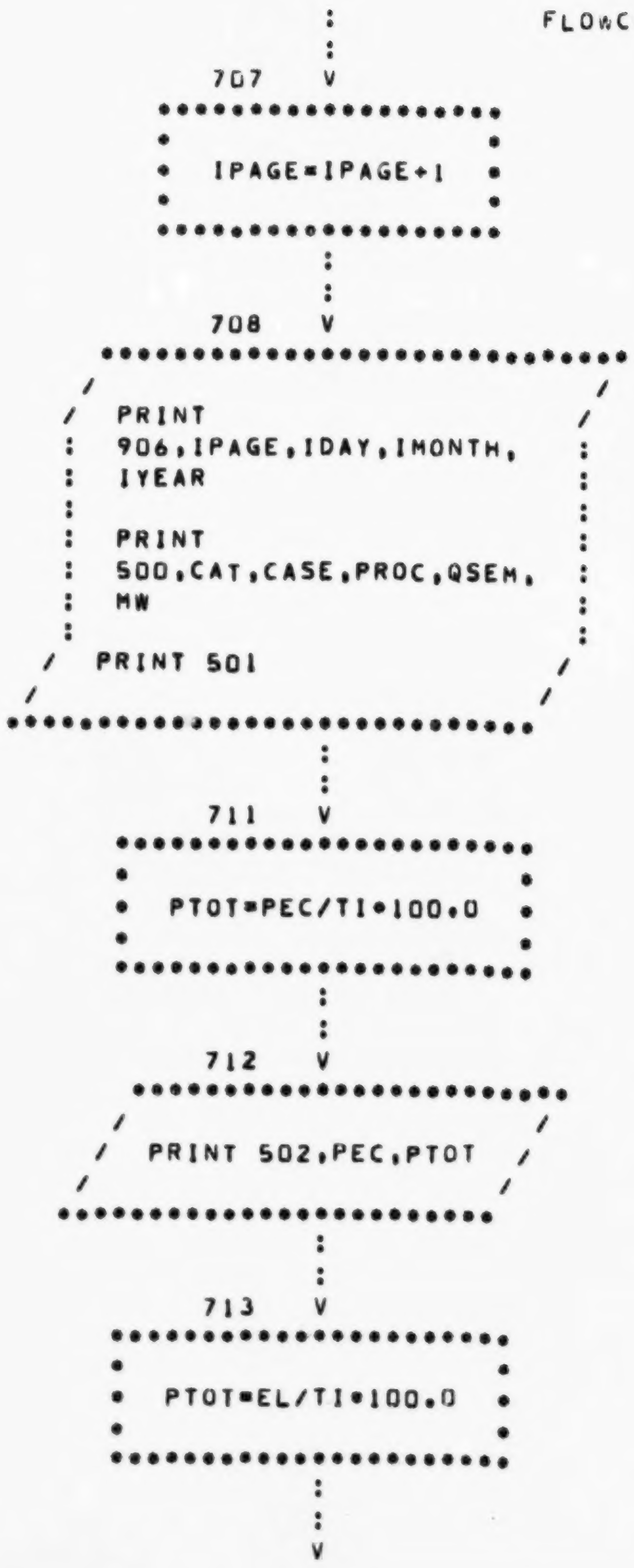
```
                           :
                           :
                     640   V
                ***************************
               /                          /
              /  PRINT 308,DIABED,HVES   /
              :                         :
              :  PRINT 309,TK,CINDEX    :
              :                         :
              :  PRINT 303              :
              :                         :
              :  PRINT 310,WS,CLIN      :
              :                         :
              :  PRINT 311,WH,COSTV     :
              :                         :
              :  PRINT 312,WD,TCOSTS    :
              :                         :
             /  PRINT 313,WV           /
            /                         /
           ***************************
                           :
 /   \                     :
( 903 )------------------->:
 \   /               648   V
                  ********************
                  *                  *
                  *  IPAGE=IPAGE+1   *
                  *                  *
                  ********************
                           :
                           :
                     649   V
               *****************************
              /                            /
             /  PRINT                     /
             :  700,IPAGE,IDAY,IMONTH,   :
             :  IYEAR                    :
             :                           :
             :  PRINT 701,EFP,PDCYCE     :
             :                           :
             :  PRINT 702,RHOGE,RHOSE    :
             :                           :
             :  PRINT 703,MUE,TKCYCE     :
             :                           :
             :  PRINT 704,NE,CINDEX      :
             :                           :
            /  PRINT 705,QAE,CYCNUM     /
           /                           /
          *****************************
                           :
                           :
                           V
```

```
                   :
                   :
          655      V
        ***************************
       /                         /
      /  PRINT 706              /
      :                         :
      :  PRINT 707              :
      :                         :
      :  PRINT 708,QICYCE,VCYCE :
      :                         :
      :  PRINT 709,DIACYE,WCE   :
      :                         :
      :  PRINT 710,EFP,DP,CCYC  :
      :                         :
      :  PRINT 711,D50          :
      :                         :
     /  PRINT 712,TCCYC        /
    /                         /
   ***************************
                   :
                   :
          662      V
                  .*.
               .*'   '*.   YES                                   / \
            .*'  IOUT.EQ.0 '*.-------------------------------->( 904 )   677
            '*.            .*'                                   \ /
               '*.       .*'
                  '*'
                   : NO
                   :
          663      V
       ********************
       *                  *
       *   IPAGE=IPAGE+1  *
       *                  *
       ********************
                   :
                   :
          664      V
        ***************************
       /                         /
      /  PRINT                  /
      :  700,IPAGE,IDAY,IMONTH, :
     /   IYEAR                 /
    /                         /
   ***************************
                   :
                   :
                   :
                   V
```

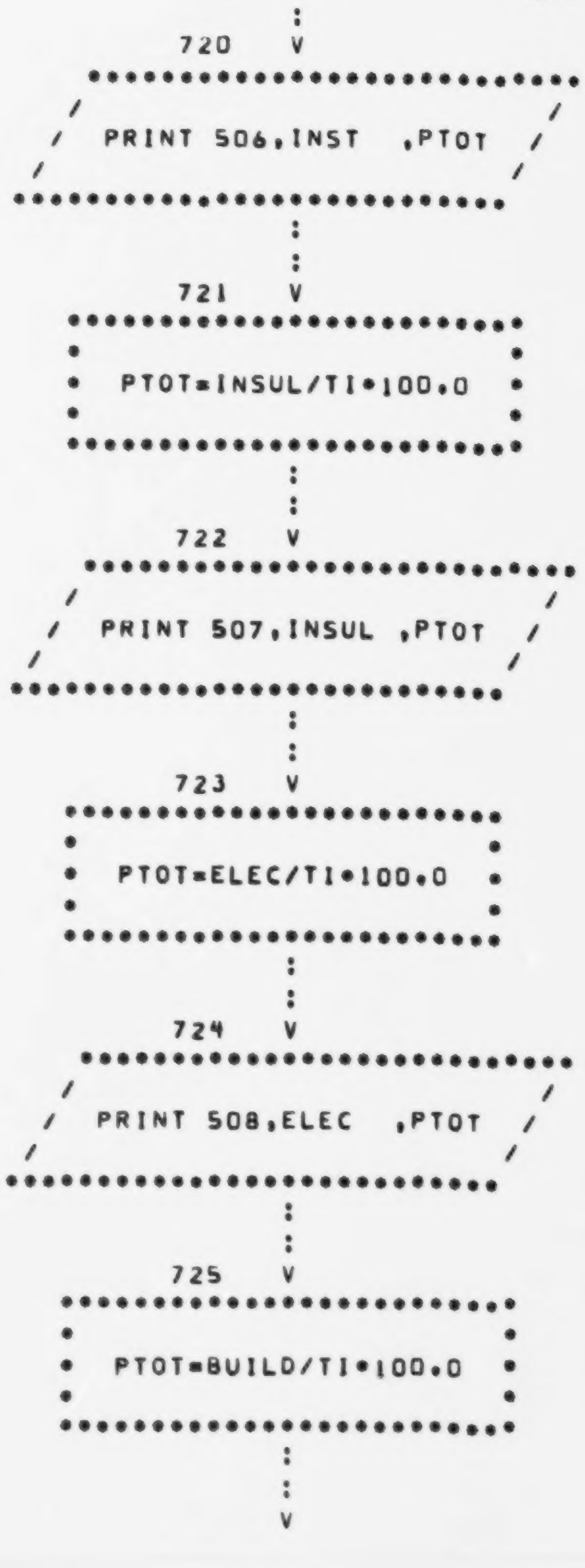

665
PRINT 713,EFP,PDCYCC
PRINT 714,RHOG,RHOSC
PRINT 715,MU,TKCYC
PRINT 704,NE,CINDEX
PRINT 716,QAC,CYCNUM
PRINT 706
PRINT 707
PRINT 717,QICYC,VCYC
PRINT 718,DIACYC,WC
PRINT 710,EFP,DP,CCYC
PRINT 711,DSD
PRINT 712,TCCYC
904
678
IFAN.EQ.1
YES
802
445
NO
679
IPAGE=IPAGE+1

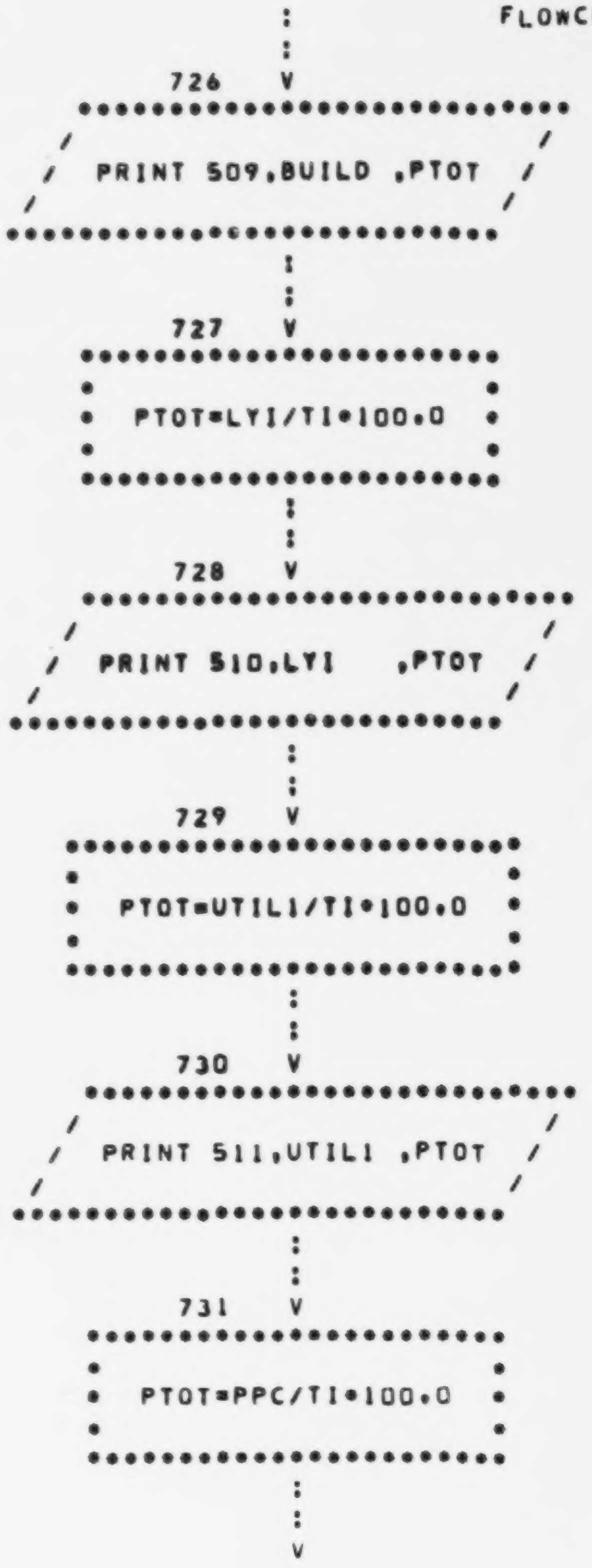
```
                 :
                 :
         680     V
     ***************************
     /                         /
    /  PRINT                  /
    :  400,IPAGE,IDAY,IMONTH, :
    :  IYEAR                  :
    :                         :
    :  PRINT                  :
    :  401,ITITLE,CINDEX,QAE  :
    :                         :
    :  PRINT 402,FSE,RHOGE    :
    :                         :
    :  PRINT 403,EFAN,DPFANE  :
    :                         :
    :  PRINT 404,FANNUM       :
    :                         :
    :  PRINT 405              :
    :                         :
    :  PRINT 406              :
    :                         :
    :  PRINT 407,QIFANE,DWFANE :
    :                         :
    :  PRINT 408,DHPFAE,FNCOST :
    :                         :
    :  PRINT 409,MOTPWE,COSTDR :
    :                         :
    :  PRINT 410,FANCAP,COSTFN :
    :                         :
   /  PRINT 411,DRVPWE,CSTFNS /
  /                         /
  ***************************
                 :
                 :
         692     V
                .*.
             .*'   '*.     YES                                       /     \
          .*'  IOUT.EQ.0  '*.--------------------------------------->( 905 )    706
          '*.             .*'                                       \     /
             '*.       .*'
                '*.*'
                 :  NO
                 :
                 :
                 :
                 :
                 :
                 :
                 :
                 V
```

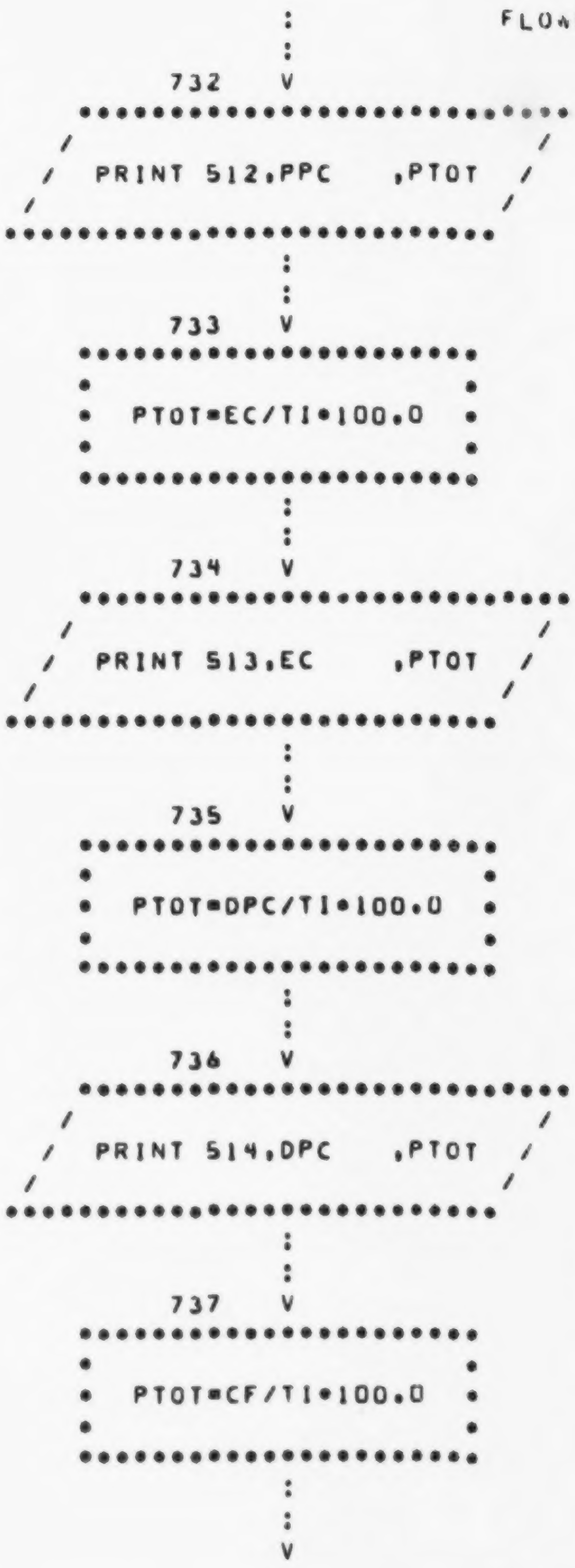
```
                        :
                        :
                 693    V
             *****************
             *               *
             *  IPAGE=IPAGE+1 *
             *               *
             *****************
                        :
                        :
                 694    V
          ***************************
          /                        /
         /  PRINT                  /
         :  400,IPAGE,IDAY,IMONTH, :
         :  IYEAR                  :
         :                         :
         :  PRINT                  :
         :  412,ITITLE,CINDEX,QAC  :
         :                         :
         :  PRINT 413,FS,RHOG      :
         :                         :
         :  PRINT 414,EFAN,DPFAN   :
         :                         :
         :  PRINT 404,FANNUM       :
         :                         :
         :  PRINT 405              :
         :                         :
         :  PRINT 406              :
         :                         :
         :  PRINT 415,QIFAN,DWFAN  :
         :                         :
         :  PRINT 416,DHPFAN,FNCOST :
         :                         :
         :  PRINT 417,MOTPWR,COSTDR :
         :                         :
         :  PRINT 410,FANCAP,COSTFN :
         :                         :
        /  PRINT 411,DRVPWE,CSTFNS /
       /                         /
       **************************
                        :
  /     \               :
 (  905  )------------->:
  \     /               :
                        :
                        :
                        :
                        :
                        :
                        V
```


707
IPAGE=IPAGE+1
708
PRINT
906,IPAGE,IDAY,IMONTH,
IYEAR
PRINT
500,CAT,CASE,PROC,QSEM,
MW
PRINT 501
711
PTOT=PEC/TI*100.0
712
PRINT 502,PEC,PTOT
713
PTOT=EL/TI*100.0

```
                   :
                   :
         714       V
          **************************
         /                         /
        /  PRINT 503,EL     ,PTOT /
       /                         /
      **************************
                   :
                   :
         715       V
          **********************
          *                    *
          *  PTOT=FP/TI*100.0  *
          *                    *
          **********************
                   :
                   :
         716       V
          **************************
         /                         /
        /  PRINT 504,FP     ,PTOT /
       /                         /
      **************************
                   :
                   :
         717       V
         ***********************
         *                     *
         *  PTOT=PIPE/TI*100.0 *
         *                     *
         ***********************
                   :
                   :
         718       V
          **************************
         /                         /
        /  PRINT 505,PIPE   ,PTOT /
       /                         /
      **************************
                   :
                   :
         719       V
         ***********************
         *                     *
         *  PTOT=INST/TI*100.0 *
         *                     *
         ***********************
                   :
                   :
                   V
```


720
PRINT 506,INST ,PTOT
721
PTOT=INSUL/TI*100.0
722
PRINT 507,INSUL ,PTOT
723
PTOT=ELEC/TI*100.0
724
PRINT 508,ELEC ,PTOT
725
PTOT=BUILD/TI*100.0


726
PRINT 509,BUILD ,PTOT
727
PTOT=LYI/TI*100.0
728
PRINT 510,LYI   ,PTOT
729
PTOT=UTILI/TI*100.0
730
PRINT 511,UTILI ,PTOT
731
PTOT=PPC/TI*100.0


732
PRINT 512,PPC ,PTOT
733
PTOT=EC/TI*100.0
734
PRINT 513,EC ,PTOT
735
PTOT=DPC/TI*100.0
736
PRINT 514,DPC ,PTOT
737
PTOT=CF/TI*100.0

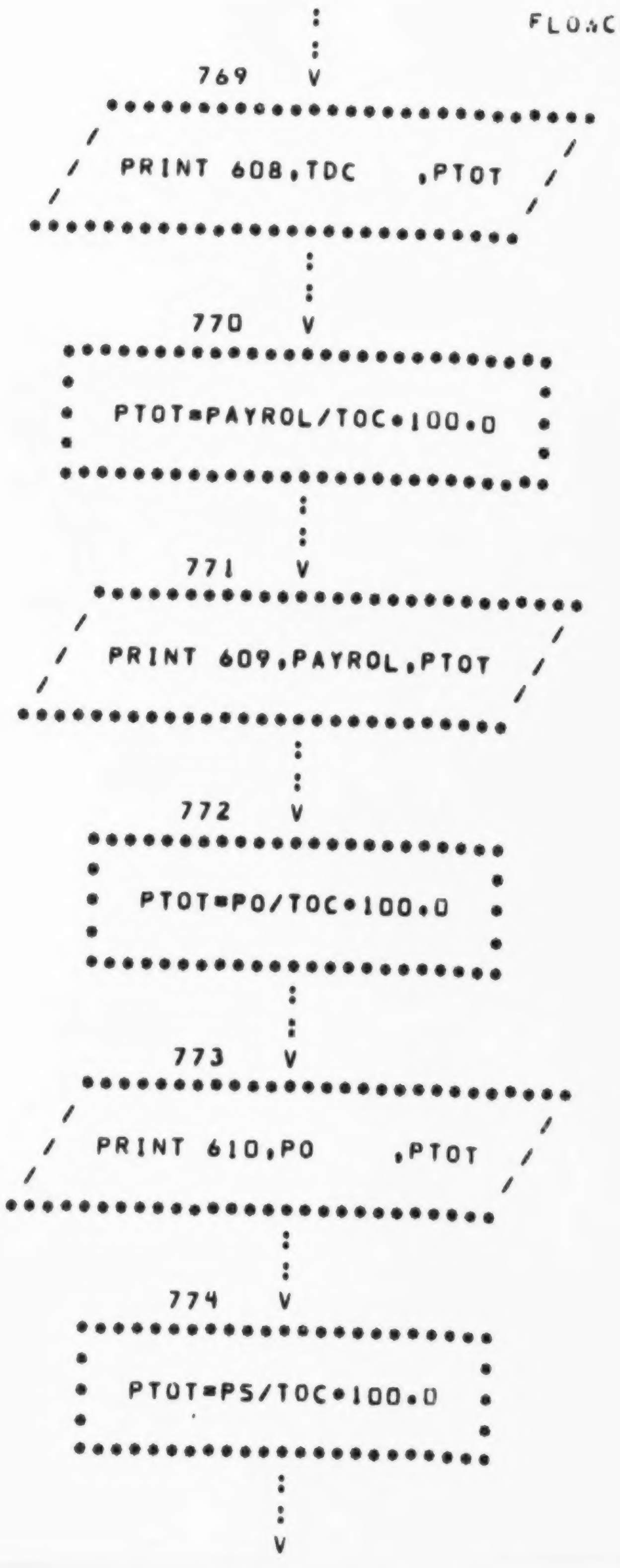
```
               :
               :
          738  V
    **************************
   /                         /
  /  PRINT 515,CF    ,PTOT  /
 /                         /
**************************
               :
               :
          739  V
   ***********************
   *                     *
   *  PTOT=CONT/TI*100.0 *
   *                     *
   ***********************
               :
               :
          740  V
    **************************
   /                         /
  /  PRINT 516,CONT  ,PTOT  /
 /                         /
**************************
               :
               :
          741  V
    **********************
    *                    *
    *  PTOT=FCC/TI*100.0 *
    *                    *
    **********************
               :
               :
          742  V
    **************************
   /                         /
  /  PRINT 517,FCC   ,PTOT  /
 /                         /
**************************
               :
               :
          743  V
    **********************
    *                    *
    *  PTOT=WCC/TI*100.0 *
    *                    *
    **********************
               :
               :
               V
```

```
                 :          FLOWCHART OF FLUID    PAGE 39
                 :
           744   V
       ..........................
      /                        /
     /  PRINT 518,WCC    ,PTOT /
    /                        /
   ..........................
                 :
                 :
           745   V
         ...............
         .             .
         .  PTOT=100.0 .
         .             .
         ...............
                 :
                 :
           746   V
       ..........................
      /                        /
     /  PRINT 519,TI     ,PTOT /
    :                         :
   /  PRINT 520,CR           /
  /                         /
 ..........................
                 :
                 :
           748   V
        ..................
        .                .
        .  IPAGE=IPAGE+1 .
        .                .
        ..................
                 :
                 :
           749   V
      ...........................
     /                         /
    /  PRINT                  /
   :  906,IPAGE,IDAY,IMONTH,  :
  /  IYEAR                   /
 /                          /
...........................
                 :
                 :
                 :
                 :
                 :
                 :
                 V
```

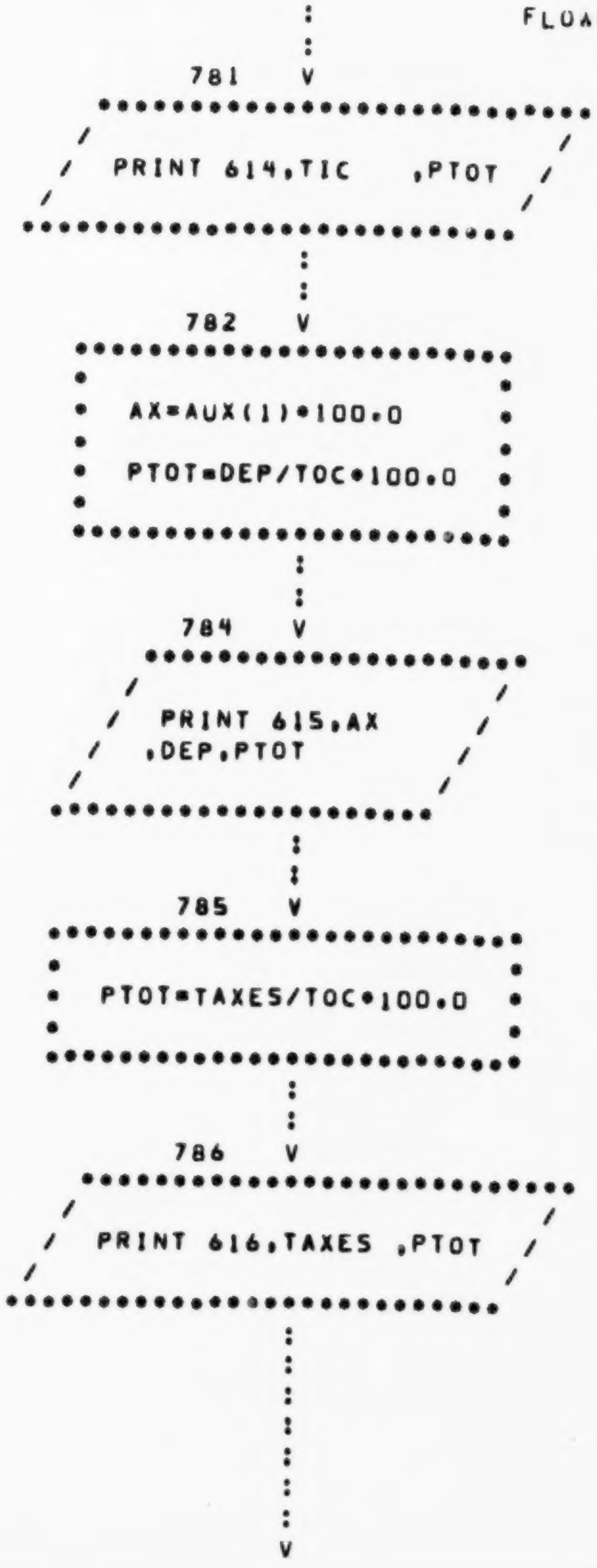
```
                     :
                     :
             750     V
          ***********************
          *                     *
          *  DY330=AUX(2)*100.0 *
          *                     *
          *  FCC1=FCC*1000.0    *
          *                     *
          ***********************
                     :
                     :
             752     V
         *****************************
        /                            /
       /  PRINT                     /
       :  600,CAT,DY330,PROC,QSEM,  :
       :  MW,FCC1                   :
       :                            :
      /  PRINT 501                 /
     /                            /
    *****************************
                     :
                     :
             754     V
          ***********************
          *                     *
          *  PTOT=RMC/TOC*100.0 *
          *                     *
          ***********************
                     :
                     :
             755     V
           *************************
          /                       /
         /  PRINT 601,RMC   ,PTOT /
        /                       /
       *************************
                     :
                     :
             756     V
          ***********************
          *                     *
          *  PTOT=DL/TOC*100.0  *
          *                     *
          ***********************
                     :
                     :
                     :
                     :
                     V
```

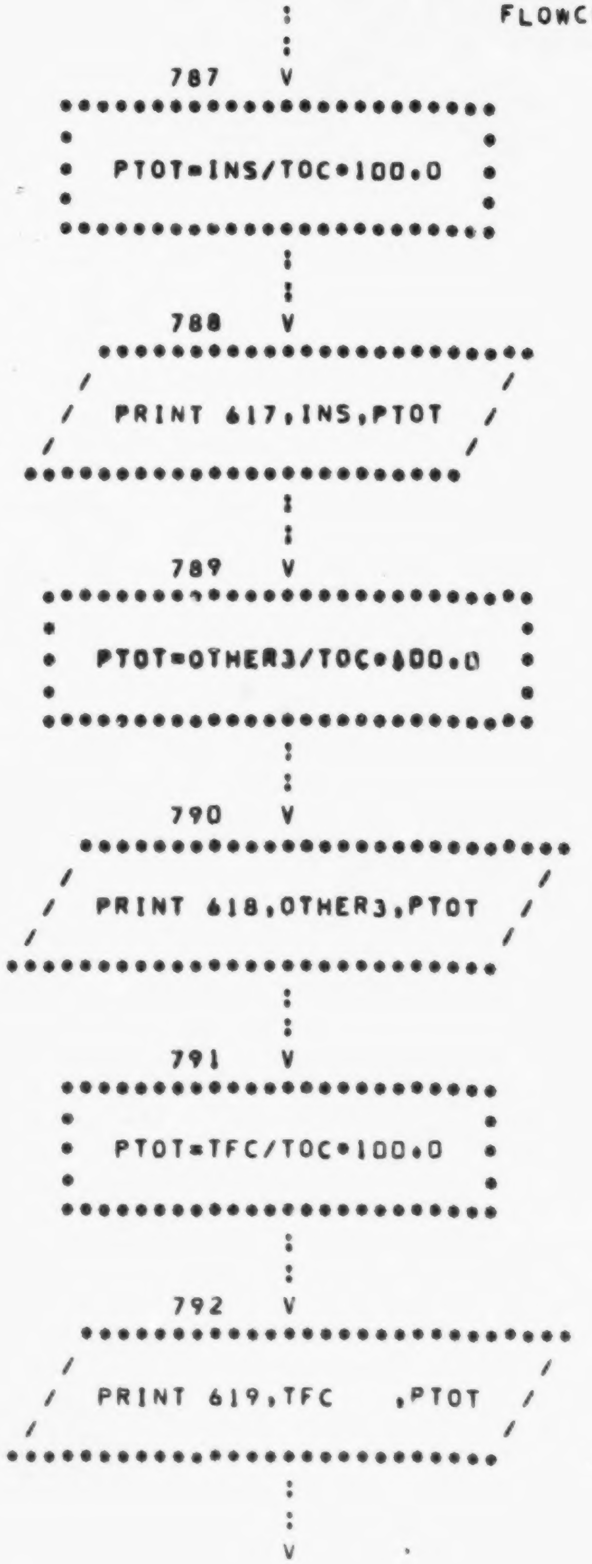
```
               :
               :
         757   V
    ***************************
   /                         /
  /  PRINT 602,DL    ,PTOT  /
 /                         /
***************************
               :
               :
         758   V
   ************************
   *                      *
   *  PTOT=SUP/TOC*100.0  *
   *                      *
   ************************
               :
               :
         759   V
    ***************************
   /                         /
  /  PRINT 603,SUP   ,PTOT  /
 /                         /
***************************
               :
               :
         760   V
   *************************
   *                       *
   *  PTOT=MAIN/TOC*100.0  *
   *                       *
   *************************
               :
               :
         761   V
    ***************************
   /                         /
  /  PRINT 604,MAIN  ,PTOT  /
 /                         /
***************************
               :
               :
         762   V
  ***************************
  *                         *
  *  PTOT=SUPPLY/TOC*100.0  *
  *                         *
  ***************************
               :
               :
               V
```

```
              :
              :
        763   V
    **************************
   /                        /
  /  PRINT 605,SUPPLY,PTOT  /
 /                        /
**************************
              :
              :
        764   V
  *************************
  *                       *
  *  PTOT=UTIL2/TOC*100.0 *
  *                       *
  *************************
              :
              :
        765   V
    **************************
   /                        /
  /  PRINT 606,UTIL2 ,PTOT  /
 /                        /
**************************
              :
              :
        766   V
  **************************
  *                        *
  *  PTOT=OTHER1/TOC*100.0 *
  *                        *
  **************************
              :
              :
        767   V
    **************************
   /                        /
  /  PRINT 607,OTHER1,PTOT  /
 /                        /
**************************
              :
              :
        768   V
   ************************
   *                      *
   *  PTOT=TDC/TOC*100.0  *
   *                      *
   ************************
              :
              :
              V
```


769
PRINT 608,TDC ,PTOT
770
PTOT=PAYROL/TOC*100.0
771
PRINT 609,PAYROL,PTOT
772
PTOT=PO/TOC*100.0
773
PRINT 610,PO ,PTOT
774
PTOT=PS/TOC*100.0

```
                :
                :
        775     V
      **************************
     /                        /
    /  PRINT 611,PS    ,PTOT /
   /                        /
  **************************
                :
                :
        776     V
     ************************
     *                      *
     *  PTOT=WSD/TOC*100.0  *
     *                      *
     ************************
                :
                :
        777     V
      ************************
     /                      /
    /  PRINT 612,WSD,PTOT  /
   /                      /
  ************************
                :
                :
        778     V
    **************************
    *                        *
    *  PTOT=OTHER2/TOC*100.0 *
    *                        *
    **************************
                :
                :
        779     V
      ***************************
     /                         /
    /  PRINT 613,OTHER2,PTOT  /
   /                         /
  ***************************
                :
                :
        780     V
     ************************
     *                      *
     *  PTOT=TIC/TOC*100.0  *
     *                      *
     ************************
                :
                :
                V
```


781
PRINT 614,TIC ,PTOT
782
AX=AUX(1)*100.0
PTOT=DEP/TOC*100.0
784
PRINT 615,AX
,DEP,PTOT
785
PTOT=TAXES/TOC*100.0
786
PRINT 616,TAXES ,PTOT


787
PTOT=INS/TOC*100.0
788
PRINT 617,INS,PTOT
789
PTOT=OTHER3/TOC*100.0
790
PRINT 618,OTHER3,PTOT
791
PTOT=TFC/TOC*100.0
792
PRINT 619,TFC ,PTOT

```
                   :
                   :
          793      V
        ***************
        *             *
        *  PTOT=100.0 *
        *             *
        ***************
                   :
                   :
          794      V
     ***************************
    /                         /
   /  PRINT 620,TOC,PTOT     /
   :                         :
  /  PRINT 621,COSTD,COSTM  /
 /                         /
***************************
                   :
                   V
                  / \
                ( 802 )    445
                  \ /
```

8.1 UNABRIDGED TECHNICAL MEMORANDUMS

8.1.3 Technical Memorandums on Economic Feasibility Studies

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

20 December 1968

G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch19

FLUIDIZED-BED SORBER DESIGN

The dry metal oxide sulfur recovery processes under consideration are composed of the following steps: 1) sorption, 2) regeneration, and 3) sulfur recovery. The most essential piece of equipment in the sorption step is the sorber. The type of sorber chosen to be used in making economic studies of dry metal oxide sulfur recovery processes was the fluidized-bed.

The fluidized-bed model used for the sorber design is based on the bubbling bed model proposed by Kunii and Levenspiel (KU-007,KU-008). This simple three-region model for the gas flow through fluidized beds views uniformly sized bubbles, surrounded by clouds and followed by wakes, rising through an emulsion of downward moving solids. The bubble diameter is calculated using equations given by Kato and Wen (KA-004). Interchange of gas occurs continuously between bubble, cloud-wake, and emulsion regions. The minimum fluidization velocity is calculated from equations given by Leva (LE-001a). Values of the ratio of superficial gas velocity to minimum fluidization velocity (U_o/U_{mf}) are used as input parameters which in turn set the required sorber diameter.

For a given conversion, reaction rate constant, particle diameter and physical properties of gas and solid, the expanded bed height can be calculated. This memorandum describes a method for calculating the expanded bed height along with the pressure drop.

The minimum fluidization mass velocity is calculated using an equation given by Leva (LE-004a).

$$G^*_{mf} = \frac{0.72\ d_p^{1.82}}{\mu^{.88}} \quad [\rho_g(\rho_s - \rho_g)]^{.94} \tag{1}$$

The Reynolds number must be checked since the above equation is valid only for Reynolds numbers less than ten. The Reynolds number is calculated using the following equation.

$$Re = \frac{d_p\ G^*_{mf}}{\mu} \tag{2}$$

If $Re > 10$, the minimum fluidization mass velocity must be corrected using correction factors given in Leva (LE-004b). The corrected value for the minimum fluidization mass velocity is given by the following equation:

$$G_{mf} = G^*_{mf} \cdot C_f \tag{3}$$

Using the corrected minimum fluidization mass velocity, the minimum fluidization voidage can be calculated from the following relationship:

$$\left(\frac{1-\epsilon_{mf}}{\epsilon_{mf}^3}\right) = \frac{.005\, d_p^2 g_c \rho_g (\rho_s - \rho_g)}{G_{mf}\, \varphi_s^2\, \mu} \tag{4}$$

A plot of $(1-\epsilon_{mf})/\epsilon_{mf}^3$ vs ϵ_{mf} was constructed and converted to equation form explicit in ϵ_{mf} in order to facilitate computer computations.

The minimum fluidization velocity can be calculated using the following mass balance equation.

$$U_{mf} = \frac{G_{mf}}{\rho_g} \tag{5}$$

From a given value for the ratio of U_o/U_{mf} along with Equation 5, the superficial gas velocity U_o can be determined. Using this value of U_o, the sorber diameter can be calculated given gas flow rate.

$$D_s = \left(\frac{4Q}{\pi U_o}\right)^{\frac{1}{2}} \tag{6}$$

The bubble diameter is calculated using the equation given by Kato and Wen (KA-004).

$$d_b = \frac{\left[\frac{6}{\pi}\left(\frac{U_o - U_{mf}}{n_o}\right)\right]^{.4}}{g_c^{.2}} + 1.4\, \rho_s d_p \left(\frac{U_o}{U_{mf}}\right) \ell \tag{7}$$

Due to the large scale equipment required to sorb the sulfur oxides from power plant stack gases, it was necessary to set limits on the bubble size. The maximum diameter that a bubble can achieve was set at 10 centimeters. The minimum bubble size is set so that the values for γ_c and γ_e will always be positive. If the initial bubble size is less than the minimum bubble size required to have a positive value for γ_e then γ_c is set equal to zero, since the bubbles in the bed are so small that the concentration of solids in the bubble cloud is negligible compared to the concentration of solids in the emulsion.

The velocity of the rising bubbles can be calculated using the equation given by Kunii and Levenspiel (KU-007).

$$U_b = U_o - U_{mf} + 0.711\ (g_c d_b)^{\frac{1}{2}} \tag{8}$$

The fraction of bed consisting of bubbles is calculated using the following equation.

$$\delta = \frac{U_o - (1-\delta)U_{mf}}{U_b} \simeq \frac{U_o - U_{mf}}{U_b} \tag{9}$$

The mass transfer coefficient between the bubble and cloud wake is given by Equation 10.

$$K_{bc} = 4.5\left(\frac{U_{mf}}{d_b}\right) + 5.85\left(\frac{D^{\frac{1}{2}} g_c^{\frac{1}{4}}}{d_b^{5/4}}\right) \qquad (10)$$

The mass transfer coefficient between the cloud and emulsion is given by the equation:

$$K_{ce} = 6.78\left(\frac{\varepsilon_{mf} D U_b}{d_b^3}\right)^{\frac{1}{2}} \qquad (11)$$

The distribution of solids among the bubble, cloud, and emulsion regions can be calculated using the following relationships:

$$\gamma_b \approx .001 \text{ to } .01 \qquad (12)$$

$$\gamma_c = (1-\varepsilon_{mf})\left[\frac{3U_{mf}/\varepsilon_{mf}}{.711(g_c d_b)^{\frac{1}{2}} - U_{mf}/\varepsilon_{mf}} + \alpha\right] \qquad (13)$$

where $\alpha = \frac{\text{volume wake}}{\text{volume bubble}} \sim .325$

$$\gamma_e = \frac{\left(1-\varepsilon_{mf}\right)\left(1-\delta\right)}{\delta} - \gamma_c - \gamma_b \qquad (14)$$

By taking the above equations and solving for the various terms along with a given conversion and kinetic reaction rate constant the fluidized-bed height can be calculated.

$$\ln \frac{C_{Abo}}{C_{Abi}} = - K_r \int_o^{L_f} \frac{\theta d\ell}{U_b} \tag{15}$$

Where $$\theta = \gamma_b + \cfrac{1}{\cfrac{K_r}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{K_r}{K_{ce}} + \cfrac{1}{\gamma_e}}}}$$

The integral in Equation 14 is solved using numerical integratio methods.

The bed voidage at the expanded bed height is given by the following:

$$\epsilon_f = 1 - (1-\delta)(1-\epsilon_{mf}) \tag{16}$$

The pressure drop through a fluidized-bed when the bed is expanded is given by Leva (LE-004c).

$$\Delta P = (9.66\times10^{-4})(L_f)(1-\epsilon_f)(\rho_s-\rho_g) \tag{17}$$

In order to prevent channeling effects Zenz and Othmer (ZE-001) recommended that the pressure drop across the distributor plate be approximately 40% of the pressure drop through the fluidized-bed. The distributor plate pressure drop was designed to be within a range of ± 10% of one-third of the fluidized-bed pressure drop.

The total sorber pressure drop is equal to the pressure drop across the distributor plate plus the pressure drop through the fluidized-bed. The distributor plate was assumed to have one inch diameter holes.

The total amount of sorbent required for the fluidized-bed can be obtained using the following equation:

$$W_s = 813\ D_s^2\ \Delta P \qquad (18)$$

From the above information it is possible to calculate the sorber diameter, the expanded bed height, the amount of sorbent required, and the pressure drop through the sorber. To obtain the total sorber vessel height, a freeboard height is added to the expanded bed height. The purpose of the freeboard is to eliminate entrainment losses. For design purposes, an analogy to flow patterns through orifices was used assuming each existing bubble to act as an orifice. The average minimum downstream distance from an orifice in a pipe where swirls, eddies, and other turbulent factors cease to cause interferences in flow measurements is five pipe diameters as described by Sterns (ST-003). At this point large spurious upward velocities capable of entraining particles will have disappeared, therefore, a freeboard (disengaging height) equal to five times the diameter of a gas bubble as it exits from the top of the fluidized bed appears to be a reasonable estimate.

The terminal velocity of the sorbent particles is calculated by the following equation.

$$U_t = \left[\frac{\pi d_p g_c \rho_s}{2.28 C_D \rho_g}\right]^{\frac{1}{2}} \qquad (19)$$

The values for the drag coefficient (C_D) for circular cylinders were obtained from a plot of drag coefficient verses Reynolds number given by Schlichting (SC-009). The terminal velocity is compared with the superficial gas velocity to make sure that the sorbent particles are not being entrained out the top of the sorber.

The sorber shell thickness was calculated using the methods set forth in the American Petroleum Institute Standard 650 (AM-001). The maximum allowable tensile stress used in the design was 15,000 lb/in^2. A joint efficiency of factor of 0.75 was used in the calculations. A maximum design pressure of 5 psig was used along with a corrosion allowance of 1/16". The shell thickness is given by the following equation.

$$t = \frac{P_d D_s}{2SE} + C = 2.22 \times 10^{-4} D_s + .159 \qquad (20)$$

The minimum shell thickness for shell plates is given in the following table.

Vessel Diameter (feet)	Nominal Thickness (inches)
Smaller than 50	3/16
50 to 120 incl.	1/4
120 to 200 incl.	5/16
Over 200	3/8

A computer program was written to calculate the sorber physical dimensions. An example of the computer printout is given in Table I. Given the sorber dimensions, a sorber purchase cost can be estimated which will be used in the overall economic study on dry metal oxide sulfur recovery processes.

Gary D. Schroeder

TABLE I

```
PAGE   9                                                                          12 FEB 1969

                                      INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                     2500000.000        DENSITY OF SOLID (LBS/FT**3)          100.000
PARTICLE DIAMETER (INCHES)                 .0200        INLET CONCENT. (MOLE PERCENT)          10.000
REACTION RATE (1/SEC)                     .10000        OUTLET CONCENT. (MOLE PERCENT)          9.500
RATIO- SUPERFICIAL TO MIN. VEL.            3.000        VOL. WAKE / VOL. BUBBLE                  .320
TEMPERATURE (DEG. F.)                    300.000        FRACTION OF SOLIDS IN BUBBLE             .000
INLET PRESSURE (PSIA)                     14.700


                                      OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                     3650941.800        INITIAL BUBBLE DIAMETER (FEET)           .389
DIAMETER OF BED (FEET)                   262.192        FINAL BUBBLE DIAMETER (FEET)             .469
HEIGHT OF BED (FEET)                        .464        INITIAL BUBBLE VEL. (FT/SEC)            3.267
HEIGHT OF VESSEL (FEET)                  131.096        FINIAL BUBBLE VEL. (FT/SEC)             3.512
THICKNESS OF SHELL (INCHES)                 .762        MIN. MASS FLUX (LBS/HR-FT**2)          72.789
BED PRESSURE DROP (IN. WATER)              3.780        MIN. FLUID VOIDAGE                       .460
DISTR. PRESS. DROP (IN. WATER)             1.262        MIN. FLUID VEL. (FT/SEC)                 .376
TOTAL PRESS. DROP (IN. WATER)              5.042        HOLES/IN.**2 IN DISTR. PLATE             .033
OUTLET PRESSURE (PSIA)                    14.518        PARTICLE TERMINAL VEL. (FT/SEC)         7.905
WEIGHT OF SORBENT (LBS)              1063617.500        SUPERFICIAL VELOCITY (FT/SEC)           1.127
```

NOMENCLATURE

C	Corrosion allowance, cm
C_f	Correction factor
C_{Abi}	Concentration of "A" in the bubble at top of the bed, $\frac{\text{g-moles}}{\text{cm}^3}$
C_{Abo}	Concentration of "A" in inlet gas stream, $\frac{\text{g-moles}}{\text{cm}^3}$
C_D	Drag coefficient
d_b	Bubble diameter, cm
d_p	Particle diameter, cm
D	Diffusion coefficient, cm^2/sec
D_s	Sorber diameter, cm
E	Joint efficiency factor, fraction
G^*_{mf}	Minimum fluidization mass velocity, g/cm^2 - sec
G_{mf}	Corrected minimum fluid velocity, g/cm^2 - sec
g_c	Gravitational constant cm/sec^2
K_{bc}	Interchange coefficient between bubble and cloud, 1/sec
K_{ce}	Interchange coefficient between cloud and emulsion, 1/sec
K_r	Reaction rate constant, 1/sec
ℓ	Height above distributor plate, cm
L_f	Height of expanded bed, cm
n_o	Holes in distributor plate, holes/cm^2
P_d	Design pressure, Atm
Δ_p	Pressure drop through sorber bed, Atm
Q	Gas flow rate, cm^3/sec
Re	Reynolds number
S	Maximum tensile stress of steel, Atm

NOMENCLATURE (continued)

t	Shell thickness, cm
U_b	Velocity of bubble, cm/sec
U_{mf}	Minimum fluidization velocity, cm/sec
U_o	Superficial gas velocity, cm/sec
U_t	Therminal velocity, cm/sec
W_s	Weight of sorbent, g

GREEK

α	Volume wake/volume bubble
γ_b	Fraction of solids in bubble
γ_c	Fraction of solids in cloud
γ^e	Fraction of solids in emulsion
δ	Fraction of bed consisting of bubbles
ϵ_f	Bed voidage at expanded height
ϵ_{mf}	Minimum fluidization voidage
φ_s	Shape factor, dimensionless
μ	Gas viscosity, g/cm-sec
ρ_g	Gas density, g/cm^3
ρ_s	Solids density, g/cm^3

BIBLIOGRAPHY

AM-001	AMERICAN PETROLEUM INSTITUTE STANDARD 650, THIRD EDITION, AMERICAN PETROLEUM INSTITUTE. DIVISION OF REFINING, 1271 AVE. OF AMERICAS, NEW YORK, NEW YORK.(JULY,1966).
KA-004	K. KATO, C. Y. YEN, 'BUBBLE ASSEMBLAGE MODEL FOR FLUIDIZED BED CATALYTIC REACTORS,' OFFICE OF COAL RESEARCH, PAPER NO. VIII, CONTRACT 14-01-0001-497, (SEPTEMBER, 1968).
KU-007	D. KUNII, O. LEVENSPIEL, 'BUBBLING BED MODEL FOR KINETIC PROCESSES IN FLUIDIZED BEDS,' I & E C PROCESS DESIGN AND DEVELOPMENT, VOL. 7, NO. 4, PP. 481-91 (OCT. 1968).
KU-008	D. KUNII, O. LEVENSPIEL, 'BUBBLING BED MODEL FOR THE FLOW OF GAS THROUGH A FLUIDIZED BED,' I & E C FUNDAMENTALS, VOL. 7, NO. 3 PP. 446-52 (AUG. 1968).
LE-004	MAX LEVA, FLUIDIZATION, MCGRAW-HILL BOOK CO., NEW YORK, (1959).
LE-004	MAX LEVA, FLUIDIZATION, MCGRAW-HILL BOOK CO., NEW YORK, (1959).
LE-004	MAX LEVA, FLUIDIZATION, MCGRAW-HILL BOOK CO., NEW YORK, (1959).
SC-009	HERMANN SCHLICHTING, BOUNDARY LAYER THEORY, 4TH EDITION, MCGRAW-HILL BOOK CO., NEW YORK, (1960).
ST-003	R. F. STEARNS, FLOW MEASUREMENT WITH ORIFICE METERS, D. VAN NOSTRAND COMPANY, INC. NEW YORK (1951).
ZE-001	F. A. ZENZ, D. F. OTHMER, FLUIDIZATION AND FLUID PARTICLE SYSTEMS, REINHOLD PUBLISHING CORP., NEW YORK (1960).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

5 February 1969 G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch14

DETERMINATION OF THE PURCHASE PRICE FOR FLUIDIZED-BED SORBERS

The dry metal oxide sulfur recovery process under consideration is composed of the following three steps: 1) sorption, 2) regeneration, and 3) sulfur recovery. The major pieces of equipment used in the sorption step are the sorber, draft fan, and sorbent fines collector.

In making an economic study of dry metal oxide sulfur recovery processes, the capital investment must be estimated. The capital investment cost is computed from the purchase price of the major pieces of equipment as discussed in T.M. 004-009-Ch11. This memorandum describes a method for calculating the purchase price of the sorber.

The sorber can be divided into the following components:

1. Cylindrical Shell
2. Two Elliptical Heads
3. Gas Distributor Plate
4. Vessel Lining-Insulation Material

The purchase price of the sorber is estimated to be the sum of the costs of the individual pieces of equipment.

I. Sorber Shell Including Heads and Gas Distributor Plate

The cost of the sorber can conveniently be estimated on the basis of weight. Approximate costs per pound for fabricated steel vessels were taken from cost information supplied by the Graver Tank Company (HO-001). The fabrication costs per pound are represented by a plot given in Figure 1.

Using Figure 1, the cost of fabrication was converted to an equation of the following form.

$$C_f' = \left[.135 - .0253 \log \left(\frac{W_s}{10^6}\right)\right] \quad (1)$$

The purchase price of steel is 0.08 dollars per pound. The fabricated cost per pound is equal to the sum of the purchase price of steel plus the cost of fabrication.

$$C_s' = .215 - .0253 \log \left(\frac{W_s}{10^6}\right) \quad (2)$$

The total weight of steel in the sorber shell plus two flat heads (the weight of an elliptical head is within 0.3% of flat heads) is given by the following equation.

$$W_{sh} = \frac{\rho_s \pi D_i t}{12} \left(H + \frac{D_i}{2}\right) \quad (3)$$

The weight of steel in the gas distributor plate (assumed 5/16 inches thick) is given by the following equation.

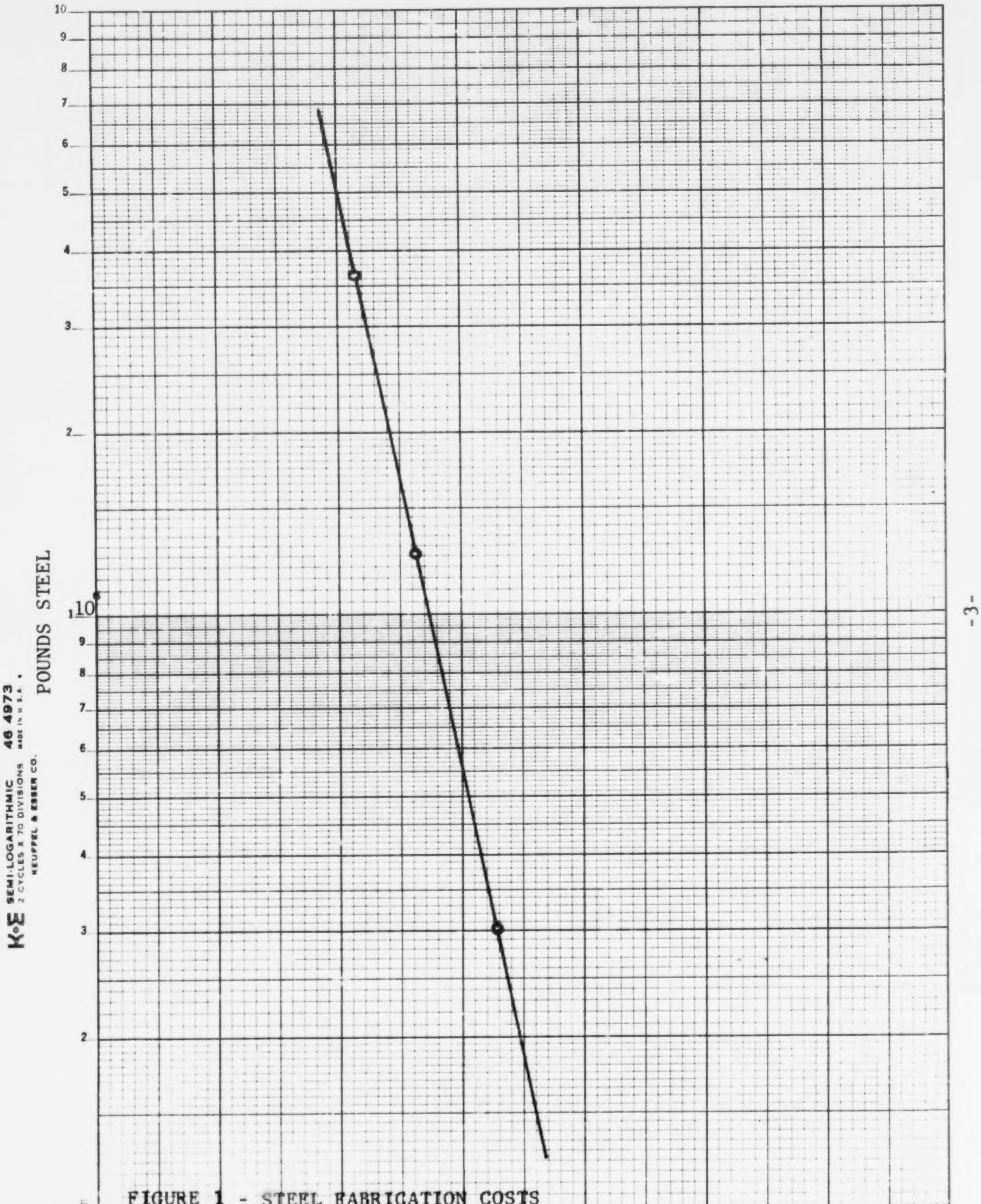


FIGURE 1 - STEEL FABRICATION COSTS

$$W_d = 10\ D_i^2 \qquad (4)$$

The total weight of the sorber vessel is composed of the weight of the shell, heads, gas distributor plate, man holes, inside ladder and other structural members, and is given by Equation 5.

$$W_s = 2.33\left[\frac{\rho_s \pi D_i t}{12}\ (H + D_i/2) + 10D_i^2\right] \qquad (5)$$

Upon substituting the pounds of steel, W_S, in Equation 2, the purchased cost of the sorber per pound is obtained.

$$C_s' = .215 - .0253\ \log\left\{\left[\frac{2.33\rho_s \pi D_i t}{12}\ (H + D_i/2)\right.\right.$$

$$\left.\left. + 23.3D_i^2\right] / 10^8\right\} \qquad (6)$$

The total purchased cost of the sorber is obtained by multiplying Equation 6 by the total weight of steel W_S (defined in Equation 5).

$$C_s = W_s\left[.215 - .0253\ \log\left(\frac{W_s}{10^8}\right)\right] \qquad (7)$$

II. Vessel Lining-Insulation

Due to the rapid movement of solid particles in a fluidized bed, the vessel is lined for abrasion resistance. The lining also serves the purpose of insulating the vessel. Perry (PE-001) gave a table of various insulating materials along with their physical properties and cost per square foot. The cost to line the inside surface area of the sorber with converted mullite was determined to be the following:

$$C_{\ell} = 0.30\pi D_i (H + D_i/2) \tag{8}$$

The marshall-Stevens cost index (AR-001) is then applied to the individual costs of each piece of equipment to update costs to current prices. The sorber vessel purchase price for the year "y" will be the sum of the individual pieces of equipment adjusted from the year of the correlation to year "y."

$$C_{sv} = C_s \cdot \frac{CI_y}{CI_{69}} + C_{\ell} \cdot \frac{CI_y}{CI_{69}} \tag{9}$$

A computer program was written to calculate the sorber purchase price given the sorber physical dimensions. An example of the sorber cost summary printout sheet is given in Table I.

```
                                  INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)          262.192         SHELL HEIGHT (FEET)                   131.096
  SHELL THICKNESS (INCHES)                 .762         CURRENT COST INDEX                    272.200


                                OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (LBS)             7833303.100         LINING COST (DOLLARS)                  76945.
  WEIGHT OF HEADS (LBS)             7833303.000         COST OF VESSEL (DOLLARS)             2466100.
  WEIGHT OF DISTR. PLATE (LBS)      1602167.500         TOTAL COST OF SORBER (DOLLARS)       2543045.
  WEIGHT OF VESSEL (LBS)           17268774.000
```

NOMENCLATURE

CI	Marshall-Stevens cost index
C_ℓ	Purchase price of vessel lining material, dollars
C'_f	Fabrication cost of steel, dollars/pound
C_s	Purchase price of vessel, dollars
C'_s	Purchase price of vessel, dollars/pound
C_{sv}	Purchase price of sorber, dollars
D_i	Inside diameter of sorber, feet
H	Height of sorber, feet
t	Metal thickness, inches
W_d	Weight of gas distributor plate, pounds
W_s	Weight of steel, pounds
W_{sh}	Weight of steel in the sorber plus heads, pounds

GREEK

ρ_s	Density of carbon steel, pounds/ft^3
π	Constant, 3.1416

BIBLIOGRAPHY

AR-001 R. S. ARIES, R. D. NEWTON, CHEMICAL ENGINEERING COST ESTIMATION, MCGRAW-HILL, NEW YORK, (1955).

HO-003 W. HOLLOWAY, GRAVER TANK COMPANY, HOUSTON, TEXAS, PRIVATE COMMUNICATION OF 27 JANUARY,1969.

PE-001 J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

31 December 1968 G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch15

DETERMINATION OF PURCHASE COST OF CYCLONE DUST-COLLECTORS AND EFFICIENT PARTICLE SIZES

The most widely used type of dust-collection equipment is the cyclone separator. Cyclones offer one of the least expensive means of dust collection from both an operating and investment viewpoint.

This memorandum describes a method for calculating the purchase cost of a standard type cyclone separator as described by Perry (PE-001) for inputs of flow rate and allowable pressure drop. The particle size removed at 98% efficiency is also calculated. The calculated cyclone costs are preliminary and will be up-dated using vendor quotations.

I. PURCHASE PRICE OF CYCLONE

The cost of the cyclone can conveniently be estimated on the basis of weight. The fabricated steel costs calculated in T.M. 004-009-Ch14 were used in computing the purchase price of the cyclone.

The pressure drop across the cyclone was taken as eight inlet velocity heads. This is given by the following equation in inches of water.

$$\Delta P = 0.024\rho_g (Q/A)^2 \qquad (1)$$

The inlet area (A) in terms of cyclone dimensions given in (PE-001) is given below.

$$A = B_c H_c \qquad (2)$$

All of the cyclone dimensions can be related to the cyclone diameter. These relationships are given in Figure 1. The inlet area in terms of cyclone diameter is given by the following:

$$A = B_c H_c = \frac{D_c}{4} \cdot \frac{D_c}{2} = \frac{D_c^2}{8} \qquad (3)$$

Upon substituting the expression for inlet area (A) in Equation 3 into Equation 1, an expression for the cyclone diameter is obtained.

$$D_c = 1.113 \left(\frac{\rho_g Q^2}{\Delta P}\right)^{0.25} \qquad (4)$$

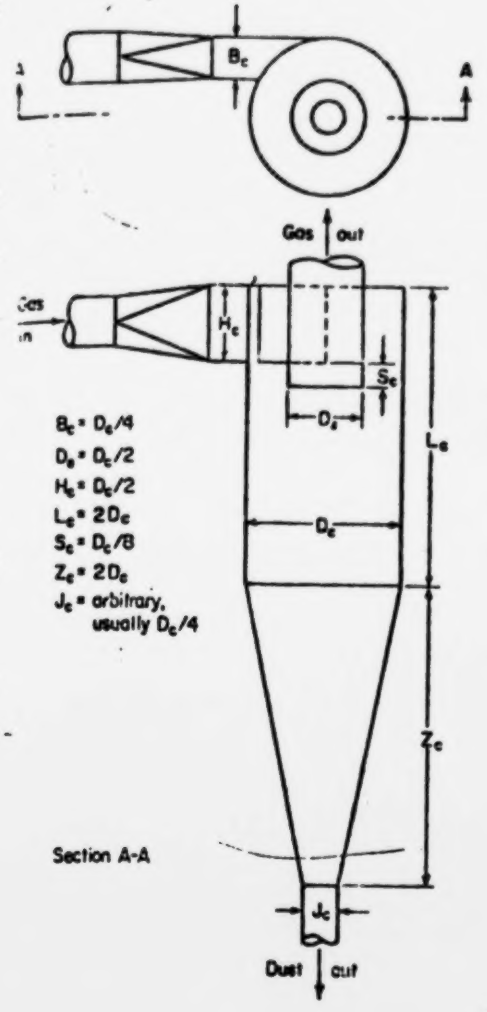

B_c
A
A
Gas out
Gas in
H_c
S_c
D_e
L_c
D_c
$B_c = D_c/4$
$D_e = D_c/2$
$H_c = D_c/2$
$L_c = 2D_c$
$S_c = D_c/8$
$Z_c = 2D_c$
J_c = arbitrary, usually $D_c/4$
Z_c
Section A-A
J_c
Dust out

FIGURE 1 - CYCLONE SEPARATOR PROPORTIONS

J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).

The cyclone diameter can now be calculated given a gas density, flow rate and specified pressure drop. The overall cyclone dimensions can also be calculated using the relationship given in Figure 1.

The total amount of steel in a cyclone separator can be determined using the calculated cyclone dimensions, wall thickness, and density of steel (assumed to be 490 lb/ft^3). The inlet rectangular duct was assumed to be half a cyclone diameter ($D_c/2$) long. The outlet duct was assumed to protrude half a cyclone diameter.

$$W_s = 500\ D_c^2\, t \qquad (5)$$

The purchase price of fabricated steel was given in Technical Memorandum 004-009-Ch14 to be the following:

$$C_s = 21.2\ (W_s)^{.689} \qquad (6)$$

Substituting the expression for W_s in equation (6) gives the estimated cyclone purchase cost.

$$C_c^1 = 21.2\ (500\ D_c^2\, t)^{.689} \qquad (7)$$

The Marshall-Stevens Cost Index (AR-001) was applied to the above equation to up-date the purchase price to current price levels.

$$C_c = 21.2\ (500\ D_c^2\, t)^{.689}\ \frac{CI_y}{CI_{57}} \qquad (8)$$

II. SEPARATION EFFICIENCY OF CYCLONES

The efficiency of a cyclone can be represented by a graph of reduced efficiency vs. particle size ratio as given in Figure 2. One point on this graph has become a useful reference point for defining the performance of a cyclone. The reference point is the particle size which gives a centrifugal efficiency of 50 percent and is known as d_{50}. The value for d_{50} can be calculated by the following equation as given by Perry (PE-001).

$$d_{50} = \left[\frac{9\mu B_c}{2\pi N_e V_c (\rho_s - \rho_g)} \right]^{.5} = \left[\frac{.0447\ \mu\ D_c^3}{NeQ(\rho_s - \rho_g)} \right] \tag{9}$$

The reduced efficiency curve given in Figure 2 can be represented by an equation given by Bradley (BR-005).

$$E = 100 \left[1 - e^{-(d/d_{50} - 0.115)^3} \right] ; \ 2\% \leq E \leq 98\% \tag{10}$$

Assuming an efficiency of 98% for the above equation, a value for the ratio d/d_{50} is obtained.

$$d/d_{50} = 1.695 \tag{11}$$

The value of d in the above expression represents the size particle having a separation efficiency of 98%.

A computer program was written to make the above calculations. An example of the computer printout summary sheet is given in Table I.

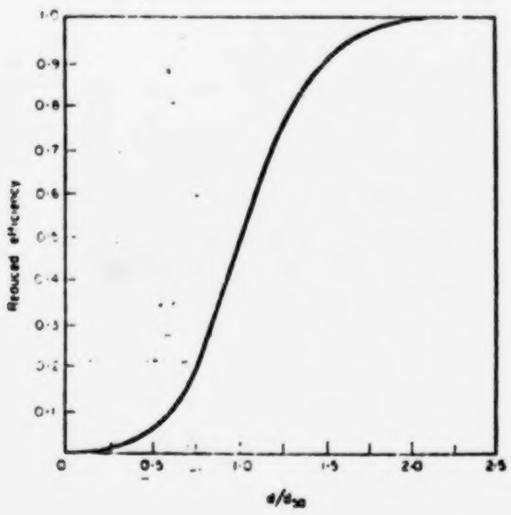


FIGURE 2 - REDUCED EFFICIENCY CURVE OF YOSHIOKA AND HOTTA

D. BRADLEY, THE HYDROCYCLONE, PERGAMON PRESS, NEW YORK (1965).

G.D. Schroeder

TABLE I

```
                                    INPUT PARAMETERS FOR CYCLONE

                                                             PRESSURE DROP (INCHES WATER)                10.000
CYCLONE REMOVAL EFFICIENCY (%)             98.000            SOLID DENSITY (LBS/FT**3)                  100.000
FLUID DENSITY (LBS/FT**3)                    .054            WALL THICKNESS (INCHES)                       .250
VISCOSITY (LBS/FT-SEC)                  .00001815            CURRENT COST INDEX                         272.200
EFFECTIVE TURNS                             3.500            NUMBER OF CYCLONES                             10.
INPUT FLOW RATE (ACFM)                3650000.000


                                    OUTPUT PARAMETERS FOR CYCLONE


                                    INDIVIDUAL CYCLONE PARAMETERS

                                                             INLET VELOCITY (FT/SEC)                     88.022
INPUT FLOW RATE (ACFM)                 365000.000            CYCLONE WEIGHT (LBS)                     69188.569
CYCLONE DIAMETER (FEET)                    23.515            COST OF EACH CYCLONE (DOLLARS)              14540.
PART. SIZE (MICRONS)= 98.% EFF.            36.313
PART. SIZE (MICRONS)= 50% EFF.             21.478

TOTAL COST OF ALL CYCLONE UNITS           145400.
```

NOMENCLATURE

A = Cross-sectional area of inlet duct to cyclone, ft^2

B_c = width of inlet duct to cyclone, ft

C_c^1 = purchased cost of cyclone based on steel fabricated costs in 1957, dollars

C_c = current purchased cost of cyclone, dollars

C_s = current purchased cost of fabricated steel, dollars

D_c = inside diameter of cyclone, ft

d = actual particle diameter, ft

d_{50} = particle diameter corresponding to a cyclone efficiency of 50%, ft

E = cyclone separation efficiency, %

N_e = effective number of turns made by a gas stream in a cyclone separator, ~3.5, dimensionless

CI   Marshall-Stevens Cost Index

Q = actual flow rate of gas being processed through cyclone, ft^3/sec

t = wall thickness, inches

V_c = inlet gas velocity to cyclone, ft/sec

ΔP = pressure drop across cyclone, inches water

ρ_g = density of gas, lb/ft^3

ρ_s = density of solids, lb/ft^3

μ = viscosity of gas, lb/ft - sec

REFERENCES

AR-001 Aries, R. S., and R. D. Newton: "Chemical Engineering Cost Estimation," p. 16, McGraw-Hill Book Company, New York, (1955).

BR-005 Bradley, D.: "The Hydrocyclone," Pergamon Press, New York. (1965).

PE-001 Perry, John H.: "Chemical Engineers' Handbook, 4th Edition, McGraw-Hill Book Company, New York, (1963).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

31 December 1968
5 February 1969, Revised

G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch15A

DETERMINATION OF PURCHASE COST OF CYCLONE DUST-COLLECTORS WITH A 98% REMOVAL EFFICIENCY

The most widely used type of dust-collection equipment is the cyclone separator. Cyclones offer one of the least expensive means of dust collection from both an operating and investment viewpoint.

This memorandum describes a method for calculating the purchase cost of a standard type cyclone separator as described by Perry (PE-001) for inputs of flow rate and allowable pressure drop. The particle size removed at 98% efficiency is also calculated.

I. PURCHASE PRICE OF CYCLONE

The cost of the cyclone can conveniently be estimated on the basis of weight. The fabricated steel costs calculated in T.M. 004-009-Ch14 were used in computing the purchase price of the cyclone.

The pressure drop across the cyclone was taken as eight inlet velocity heads. This is given by the following equation in inches of water.

$$\Delta P = 0.024\rho_g (Q/A)^2 \qquad (1)$$

The inlet area (A) in terms of cyclone dimensions given in (PE-001) is given below.

$$A = B_c H_c \qquad (2)$$

All of the cyclone dimensions can be related to the cyclone diameter. These relationships are given in Figure 1. The inlet area in terms of cyclone diameter is given by the following:

$$A = B_c H_c = \frac{D_c}{4} \cdot \frac{D_c}{2} = \frac{D_c^2}{8} \qquad (3)$$

Upon substituting the expression for inlet area (A) in Equation 3 into Equation 1, an expression for the cyclone diameter is obtained.

$$D_c = 1.113 \left(\frac{\rho_g Q^2}{\Delta P}\right)^{0.25} \qquad (4)$$

The cyclone diameter can now be calculated given a gas density, flow rate and specified pressure drop. The overall cyclone dimensions can also be calculated using the relationship given in Figure 1.

The total amount of steel in a cyclone separator can be determined using the calculated cyclone dimensions, wall thickness (3/16"), and density of steel (assumed to be 490 lb/ft^3). The inlet rectangular duct was assumed to be half a cyclone diameter ($D_c/2$) long. The outlet duct was assumed to protrude half a cyclone diameter. The compression rings, supports, and other structural members were assumed to be equal to 25% of the cyclone weight.

$$W_s = 625\ D_c^2 t \qquad (5)$$

The purchase price of fabricated steel was given in T.M. 004-009-Ch14 to be the following:

$$C_s = W_s\left[0.215 - .0253 \log\left(\frac{W_s}{10^6}\right)\right] \qquad (6)$$

Substituting the expression for W_s in Equation 6 gives the estimated cyclone purchase cost.

$$C_c' = 625\ D_c^2 t\left[.215 - .0253 \log\left(\frac{625 D_c^2 t}{10^6}\right)\right] \qquad (7)$$

The Marshall-Stevens Cost Index (AR-001) can be applied to the above equation to up-date the purchase price to current price levels.

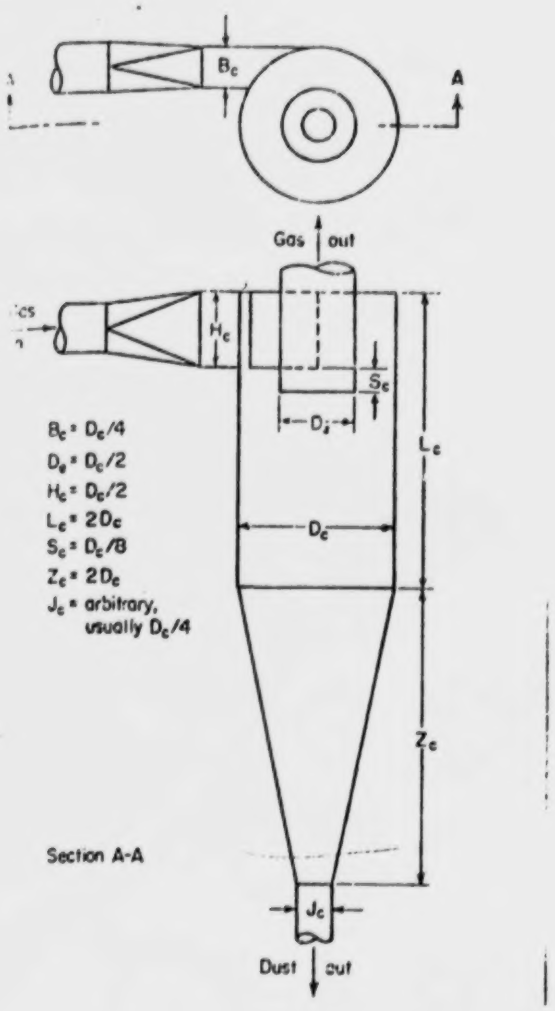

B_c
A
Gas out
H_c
S_c
D_e
L_c
$B_c = D_c/4$
$D_e = D_c/2$
$H_c = D_c/2$
$L_c = 2D_c$
$S_c = D_c/8$
$Z_c = 2D_c$
J_c = arbitrary, usually $D_c/4$
D_c
Z_c
Section A-A
J_c
Dust out

FIGURE 1 - CYCLONE SEPARATOR PROPORTIONS

J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).

$$C_c = 625\ D_c^2 t\left[.215 - .0253\ \log\left(\frac{625 D_c^2 t}{10^6}\right)\right]\frac{CI_y}{CI_{69}} \qquad (8)$$

II. SEPARATION EFFICIENCY OF CYCLONES

The efficiency of a cyclone can be represented by a graph of reduced efficiency vs. particle size ratio as given in Figure 2. One point on this graph has become a useful reference point for defining the performance of a cyclone. The reference point is the particle size which gives a centrifugal efficiency of 50 percent and is known as d_{50}. The value for d_{50} can be calculated by the following equation as given by Perry (PE-001).

$$d_{50} = \left[\frac{9\mu B_c}{2\pi N_e V_c(\rho_s - \rho_g)}\right]^{.5} = \left[\frac{.0447\ \mu\ D_c^3}{NeQ(\rho_s - \rho_g)}\right] \qquad (9)$$

The reduced efficiency curve given in Figure 2 can be represented by an equation given by Bradley (BR-005).

$$E = 100\left[1 - e^{-(d/d_{50} - 0.115)^3}\right];\ 2\% \leq E \leq 98\% \qquad (10)$$

Assuming an efficiency of 98% for the above equation, a value for the ratio d/d_{50} is obtained.

$$d/d_{50} = 1.695 \qquad (11)$$

The value of d in the above expression represents the size particle having a separation efficiency of 98%.

A computer program was written to make the above calculations. An example of the computer printout summary sheet is given in Table I.

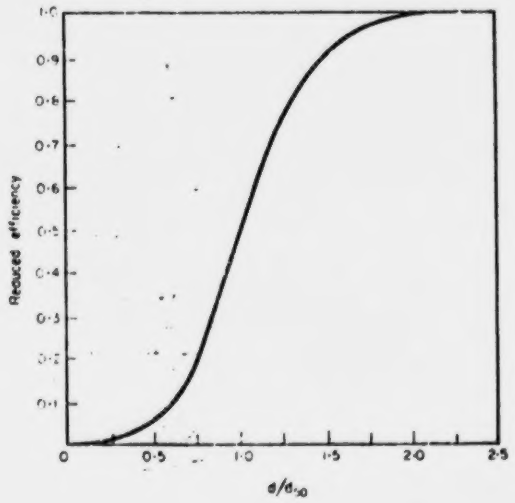


FIGURE 2 - REDUCED EFFICIENCY CURVE OF YOSHIOKA AND HOTTA

D. BRADLEY, THE HYDROCYCLONE, PERGAMON PRESS, NEW YORK (1965).

G.D. Schroeder

```
                                         INPUT PARAMETERS FOR CYCLONE

  CYCLONE REMOVAL EFFICIENCY (%)             98.000          PRESSURE DROP (INCHES WATER)            5.000
  FLUID DENSITY (LBS/FT**3)                    .054          SOLID DENSITY (LBS/FT**3)             100.000
  VISCOSITY (LBS/FT-SEC)                 .00001593           WALL THICKNESS (INCHES)                 .250
  EFFECTIVE TURNS                             3.500          CURRENT COST INDEX                    272.200
  INPUT FLOW RATE (ACFM)                3650941.800          NUMBER OF CYCLONES                         2.


                                         OUTPUT PARAMETERS FOR CYCLONE


                                        INDIVIDUAL CYCLONE PARAMETERS

  INPUT FLOW RATE (ACFM)                1825470.900          INLET VELOCITY (FT/SEC)                62.252
  CYCLONE DIAMETER (FEET)                    62.533          CYCLONE WEIGHT (LBS)               611594.560
  PART. SIZE (MICRONS)- 98.% EFF.            65.971          COST OF EACH CYCLONE (DOLLARS)        229103.
  PART. SIZE (MICRONS)- 50% EFF.             39.020

  TOTAL COST OF ALL CYCLONE UNITS           458206.
```

NOMENCLATURE

A = Cross-sectional area of inlet duct to cyclone, ft^2

B_c = width of inlet duct to cyclone, ft

C_c^1 = purchased cost of cyclone based on steel fabricated costs in January, 1969, dollars

C_c = current purchased cost of cyclone, dollars

C_s = current purchased cost of fabricated steel, dollars

D_c = inside diameter of cyclone, ft

d = actual particle diameter, ft

d_{50} = particle diameter corresponding to a cyclone efficiency of 50%, ft

E = cyclone separation efficiency, %

N_e = effective number of turns made by a gas stream in a cyclone separator, ~3.5, dimensionless

CI = Marshall-Stevens Cost Index

Q = actual flow rate of gas being processed through cyclone, ft^3/sec

t = wall thickness, inches

V_c = inlet gas velocity to cyclone, ft/sec

ΔP = pressure drop across cyclone, inches water

ρ_g = density of gas, lb/ft^3

ρ_s = density of solids, lb/ft^3

μ = viscosity of gas, lb/ft - sec

BIBLIOGRAPHY

AR-001 R. S. ARIES, R. D. NEWTON, CHEMICAL ENGINEERING COST ESTIMATION, MCGRAW-HILL, NEW YORK, (1955).

BR-005 D. BRADLEY, THE HYDROCYCLONE, PERGAMON PRESS, NEW YORK (1965).

PE-001 J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

31 December 1968

P. S. Lowell
G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch12

ESTIMATE OF FORCED-DRAFT FAN COSTS

This memorandum gives the computational procedure for estimating the purchase price of forced-draft fans such as are used to move air through power boilers. The technique is based upon estimating the cost of the fan and adding to this the cost of an electric motor driver. Only input flow rate, density, and pressure rise need be specified.

The cost correlations used were based upon data available at the time of their publication. These data are updated by applying the Marshall-Stevens cost index factors described by Aries and Newton (Ar-1).

The valid range of the driver cost estimation method was 150 to 10,000 hp. While the valid range of the fan (wheel and housing) cost estimation method was given as 30,000 to 150,000 scfm and 10 to 20 inches of water, it has proven to be valid for a 340,000 scfm, 20 inches of water fan.

I. FAN COST (Wheel and Housing Only)

It has been shown by Prater and Antonacci (Pr-1) that the cost of fans may be estimated from the wheel diameter. They presented a method for estimating the wheel diameter from the inlet flow rate, fluid density, and pressure rise. The fan price was determined for a 1200 RPM, double width, double inlet fan. This is typical of large applications.

Prater and Antonacci define the following quantities in order to calculate the whell diameter, D.

$$ESP = (SP)\ (0.075)\ /\ \rho \qquad (1)$$

$$N_s = \frac{NQ^{\frac{1}{2}}}{(ESP)^{3/4}} \qquad (2)$$

$$D = \frac{KQ^{\frac{1}{2}}}{(ESP)^{\frac{1}{4}}} \qquad (3)$$

The symbols are defined in the nomenclature. The factor, K, was given graphically as a function of specific speed. TRACOR converted this graph into equation form to facilitate computerized calculations (see Equation 4). Equation 4 is compared with the original curve in Figure 1.

$$K = 1450\ (N_s)^{-0.778} \qquad (4)$$

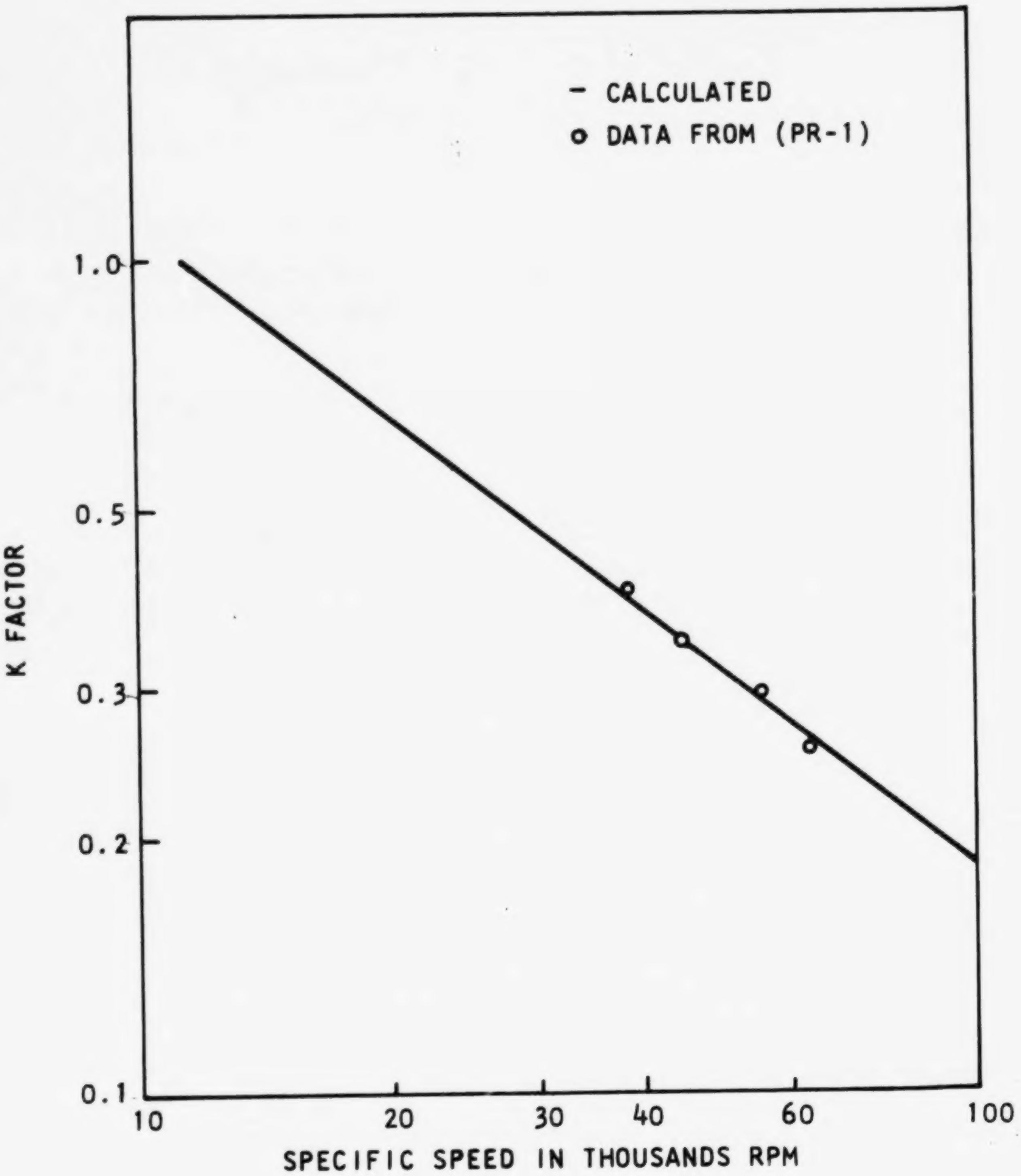


FIG. 1 - FAN RATING FACTOR

TRACOR DWG. A6-164-4
M12/23/68 NS/SCHRODER

Prater and Antonacci give the fan price as a function of wheel diameter in their Table I (Pr-1). TRACOR has fitted the data for 1200 RPM, double width and double inlet fans in the form of Equation 5 (corrected to year "y" prices).

$$C_f = 0.354(D)^{2.58}(CI_y)/(CI_{81}) \tag{5}$$

The tabular data are compared with Equation 5 in Figure 2.

From the above information the price of the fan wheel and housing may be calculated. The power required to drive the fan is also needed. The brake horsepower required may be calculated from Equation 6.

$$BHP = 0.000157Q(TP)/E_f \tag{6}$$

The input electrical power required to drive the fan accounts for the motor efficiency, E_m.

$$IP = 0.748(BHP)/E_m \tag{7}$$

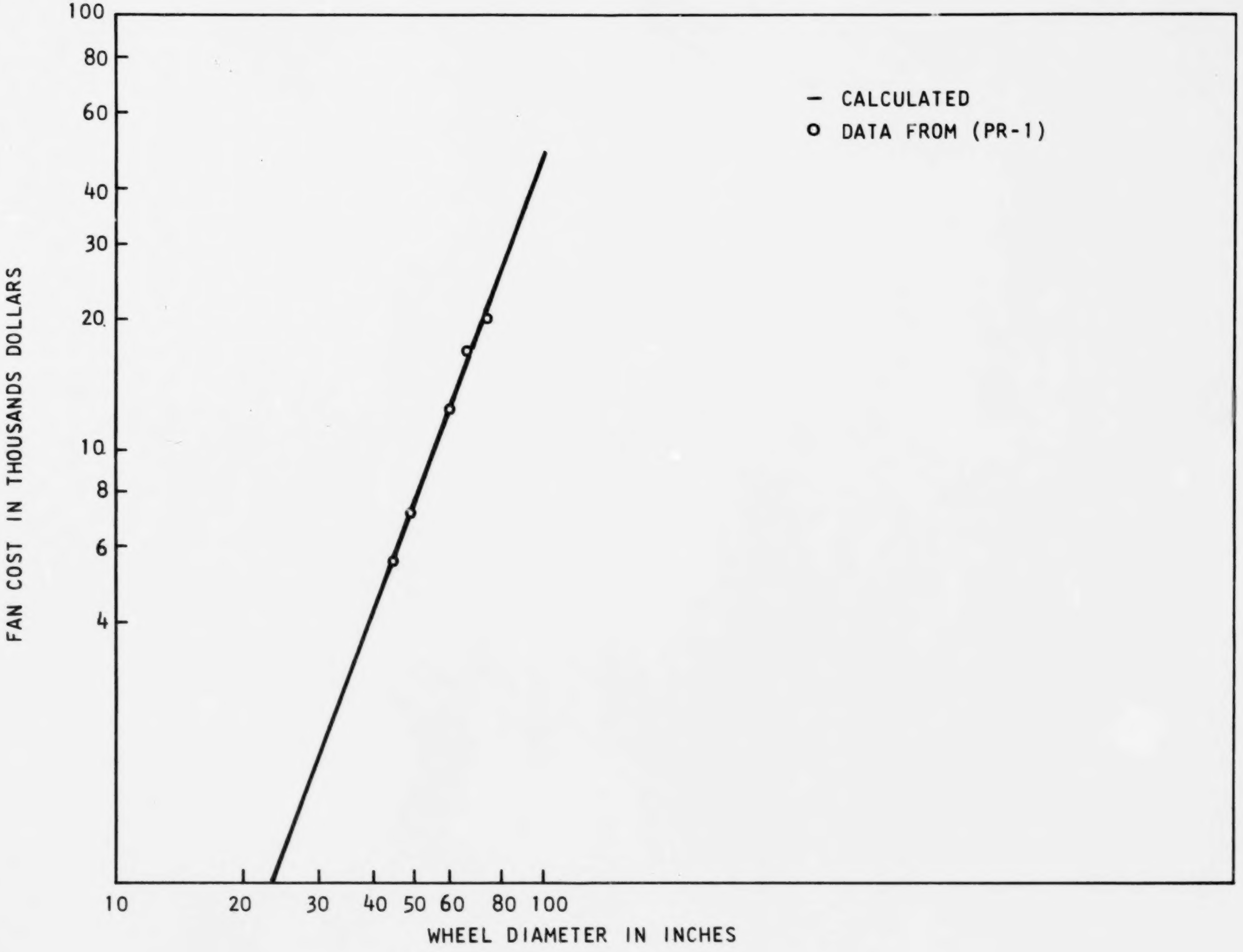


FIG. 2 - DRAFT FAN COSTS

TRACOR DWG. A6-164-3
M12/23/68 NS/SCHRODER

II. ELECTRIC MOTOR COST

The purchase price of electric motors was calculated by the method outlined by Olson and McKelvy (01-1). They present their data in graphical form. Their Figure 1 data for 1200 RPM, squirrel cage induction motors, 3-phase, 60 cycle motors at the most economical standard voltage and corrected to year "y" prices are given in equation form below.

$$C_m = 15.12\ (MHP)^{0.95}\ (CI_y)/(CI_{67}) \qquad (8)$$

The horsepower rating of the motor must be matched to the maximum horsepower that the fan might require under any flow conditions at the rated speed. This is usually about 35% more than the required fan horsepower. Hence the motor horsepower is:

$$MHP = 1.35(BHP) \qquad (9)$$

III. TOTAL COST

The total purchase price of the fan unit is the sum of the fan and motor.

$$C_t = C_f + C_m \tag{10}$$

All of the above equations may be combined to yield one equation in terms of the input variables.

$$C_t = 33.3 \left\{ Q^{0.286} \left[(SP)\ (0.075)/\rho \right]^{0.85} \frac{CI_y}{CI_{81}} \right\} + 0.00368 \left[\frac{1.35Q(TP)}{E_f} \right]^{0.95} \frac{CI_y}{CI_{87}} \tag{11}$$

The above equations were programmed for TRACOR's UNIVAC 1108 Computer. A sample case was run comparing the actual cost of the forced-draft fan purchased by the City of Austin in 1963 with the cost estimated by the above technique. The actual cost was $32,000 and the estimated cost was $33,825. The estimation calculations are attached.

P J Rowell

G. D. Schroeder

```
                                                                 20 DEC 68      PAGE      1


                                    INPUT VARIABLES FOR FANCST


COST INDEX AS OF JANUARY 1963           239.2       TOTAL FAN CAPACITY (ACFM)          340000.0
FAN SPEED (RPM)                        1200.0       AIR DENSITY (LBS/FT**3)                .075
OVERALL EFFICIENCY                       .850       FAN PRESSURE DROP (IN. WATER)          20.0
NUMBER OF FAN UNITS                        1.


                                FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                   INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)                  340000.0       WHEEL DIAMETER (INCHES)               66.59
DRIVER BRAKE HORSEPOWER                1256.0       FAN COST (DOLLARS)                   16616.
ACTUAL DRIVER HORSEPOWER               1823.2       MOTOR COST (DOLLARS)                 17209.
FRACTIONAL CAPACITY PER FAN              1.00       EACH FAN UNIT COST (DOLLARS)         33825.


KILOWATTS REQUIRED BY DRIVER(S)         936.6       COST - ALL FAN UNITS (DOLLARS)       33825.
```

NOMENCLATURE

BHP	fan brake horsepower, HP
C_f	purchase price of fan wheel and housing, dollars
C_m	purchase price of electric motor driver, dollars
C_t	total purchase price of fan unit, dollars
CI	cost index factor
D	fan wheel diameter, inches
E_f	fan efficiency, fraction
E_m	motor efficiency, fraction
ESP	equivalent static pressure, inches of water
IP	input power to fan motor, Kw
K	fan factor
MHP	rated motor horsepower, HP
N	motor speed, RPM
N_s	fan specific speed, RPM
Q	fluid flow rate, ACFM
SP	static pressure rise, inches of water
TP	total pressure rise across fan, plus inlet velocity head, inches of water
GREEK	
ρ	fluid density, lb/cu. ft.

REFERENCES

(AR-001) Aries, R. S., and R. D. Newton, Chemical Engineering Cost Estimation, p.16, McGraw-Hill Book Company, New York, (1955).

(OL-001) Olson, C. R., and E. S. McKelvy: "How to Specify and Cost Estimate Electric Motors," Hydrocarbon Processing, 46, (10) 117-34 (Oct. 1967).

(PR-001) Prater, N. H., and D. W. Antonacci: "Estimate Forced-Draft Fan Costs," Hydrocarbon Processing and Petroleum Refiner, 40, (7), 129-39, (July, 1961).

TABLE I

ESTIMATED FAN COSTS

Q 1000 ACFM	ΔP Inches H_2O	POWER REQUIREMENT kw	PURCHASE[+] COST Dollars	Dollars/1000 ACFM-In.-H_2O	OPERATING COST Mills/Yr.-ACFM-In.-H_2O
1250	5	861	26,510	4.24	6.55
1250	10	1,722	50,119	4.01	6.55
1250	20	3,443	94,853	3.79	6.55
1250	40	6,887	179,691	3.60	6.55
2500	5	1,722	45,198	3.61	6.55
2500	10	3,443	85,983	3.43	6.55
2500	20	6,887	163,703	3.27	6.55
2500	40	13,773	311,919	3.12	6.55
340[x]	20	937	38,500	5.67	6.55
2500[*]	1		50,000	20.0	10.00

x Data from Austin Power Plant

* Data from the Department of Health, Education, and Welfare

+ Purchase cost for 1968

```
                                                                19 DEC 68     PAGE     1

                                     INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968               272.0         TOTAL FAN CAPACITY (ACFM)            1250000.0
FAN SPEED (RPM)                            1200.0         AIR DENSITY (LBS/FT**3)                   .075
OVERALL EFFICIENCY                           .850         FAN PRESSURE DROP (IN. WATER)              5.0
NUMBER OF FAN UNITS                            1.

                                FAN AND DRIVER MOTOR OUTPUT PARAMETERS

                                    INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)                     1250000.0         WHEEL DIAMETER (INCHES)                  48.62
DRIVER BRAKE HORSEPOWER                    1154.4         FAN COST (DOLLARS)                       8448.
ACTUAL DRIVER HORSEPOWER                   1675.8         MOTOR COST (DOLLARS)                    18062.
FRACTIONAL CAPACITY PER FAN                  1.00         EACH FAN UNIT COST (DOLLARS)            26510.

KILOWATTS REQUIRED BY DRIVER(S)             860.9         COST - ALL FAN UNITS (DOLLARS)          26510.
```

```
                                                                          19 DEC 68     PAGE     1


                                    INPUT VARIABLES FOR FANCST


COST INDEX AS OF JANUARY 1968          272.0      TOTAL FAN CAPACITY (ACFM)          1250000.0
FAN SPEED (RPM)                       1200.0      AIR DENSITY (LBS/FT**3)                 .075
OVERALL EFFICIENCY                      .850      FAN PRESSURE DROP (IN. WATER)           10.0
NUMBER OF FAN UNITS                       1.


                              FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                 INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)                1250000.0      WHEEL DIAMETER (INCHES)                61.20
DRIVER BRAKE HORSEPOWER               2308.8      FAN COST (DOLLARS)                    15227.
ACTUAL DRIVER HORSEPOWER              3351.5      MOTOR COST (DOLLARS)                  34893.
FRACTIONAL CAPACITY PER FAN             1.00      EACH FAN UNIT COST (DOLLARS)          50119.

KILOWATTS REQUIRED BY DRIVER(S)       1721.7      COST - ALL FAN UNITS (DOLLARS)        50119.
```

```
                                                                  19 DEC 68      PAGE      1

                                   INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968          272.0          TOTAL FAN CAPACITY (ACFM)            1250000.0
FAN SPEED (RPM)                       1200.0          AIR DENSITY (LBS/FT**3)                   .075
OVERALL EFFICIENCY                      .850          FAN PRESSURE DROP (IN. WATER)             20.0
NUMBER OF FAN UNITS                       1.


                            FAN AND DRIVER MOTOR OUTPUT PARAMETERS

                                INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)                1250000.0          WHEEL DIAMETER (INCHES)                  77.04
DRIVER BRAKE HORSEPOWER               4617.6          FAN COST (DOLLARS)                      27445.
ACTUAL DRIVER HORSEPOWER              6703.0          MOTOR COST (DOLLARS)                    67408.
FRACTIONAL CAPACITY PER FAN             1.00          EACH FAN UNIT COST (DOLLARS)            94853.

KILOWATTS REQUIRED BY DRIVER(S)       3443.4          COST - ALL FAN UNITS (DOLLARS)          94853.
```

```
                                                         19 DEC 68     PAGE     1


                                 INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968          272.0        TOTAL FAN CAPACITY (ACFM)          1250000.0
FAN SPEED (RPM)                       1200.0        AIR DENSITY (LBS/FT**3)                 .075
OVERALL EFFICIENCY                      .850        FAN PRESSURE DROP (IN. WATER)           40.0
NUMBER OF FAN UNITS                       1.


                            FAN AND DRIVER MOTOR OUTPUT PARAMETERS

                               INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)                1250000.0        WHEEL DIAMETER (INCHES)                96.98
DRIVER BRAKE HORSEPOWER               9235.3        FAN COST (DOLLARS)                    49466.
ACTUAL DRIVER HORSEPOWER             13406.1        MOTOR COST (DOLLARS)                 130224.
FRACTIONAL CAPACITY PER FAN             1.00        EACH FAN UNIT COST (DOLLARS)         179691.

KILOWATTS REQUIRED BY DRIVER(S)       6886.9        COST - ALL FAN UNITS (DOLLARS)       179691.
```

```
                                                                   19 DEC 68     PAGE      1

                                   INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968            272.0        TOTAL FAN CAPACITY (ACFM)          2500000.0
FAN SPEED (RPM)                         1200.0        AIR DENSITY (LBS/FT**3)                 .075
OVERALL EFFICIENCY                        .850        FAN PRESSURE DROP (IN. WATER)           10.0
NUMBER OF FAN UNITS                         1.


                              FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                 INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)                  2500000.0        WHEEL DIAMETER (INCHES)                66.14
DRIVER BRAKE HORSEPOWER                 4617.6        FAN COST (DOLLARS)                    18575.
ACTUAL DRIVER HORSEPOWER                6703.0        MOTOR COST (DOLLARS)                  67408.
FRACTIONAL CAPACITY PER FAN               1.00        EACH FAN UNIT COST (DOLLARS)          85983.

KILOWATTS REQUIRED BY DRIVER(S)         3443.4        COST - ALL FAN UNITS (DOLLARS)        85983.
```

```
                                                                          19 DEC 68     PAGE      1

                                     INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968           272.0          TOTAL FAN CAPACITY (ACFM)           2500000.0
FAN SPEED (RPM)                        1200.0          AIR DENSITY (LBS/FT**3)                  .075
OVERALL EFFICIENCY                       .850          FAN PRESSURE DROP (IN. WATER)             5.0
NUMBER OF FAN UNITS                        1.

                               FAN AND DRIVER MOTOR OUTPUT PARAMETERS

                                   INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)                 2500000.0          WHEEL DIAMETER (INCHES)                 52.55
DRIVER BRAKE HORSEPOWER                2308.8          FAN COST (DOLLARS)                     10305.
ACTUAL DRIVER HORSEPOWER               3351.5          MOTOR COST (DOLLARS)                   34893.
FRACTIONAL CAPACITY PER FAN              1.00          EACH FAN UNIT COST (DOLLARS)           45198.

KILOWATTS REQUIRED BY DRIVER(S)        1721.7          COST - ALL FAN UNITS (DOLLARS)         45198.
```

```
                                                               19 DEC 68     PAGE     1


                                  INPUT VARIABLES FOR FANCST


COST INDEX AS OF JANUARY 1968             272.0        TOTAL FAN CAPACITY (ACFM)            2500000.0
FAN SPEED (RPM)                          1200.0        AIR DENSITY (LBS/FT**3)                   .075
OVERALL EFFICIENCY                         .850        FAN PRESSURE DROP (IN. WATER)             20.0
NUMBER OF FAN UNITS                          1.


                             FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                 INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)                   2500000.0        WHEEL DIAMETER (INCHES)                  83.26
DRIVER BRAKE HORSEPOWER                  9235.3        FAN COST (DOLLARS)                      33479.
ACTUAL DRIVER HORSEPOWER                13406.1        MOTOR COST (DOLLARS)                   130224.
FRACTIONAL CAPACITY PER FAN                1.00        EACH FAN UNIT COST (DOLLARS)           163703.


KILOWATTS REQUIRED BY DRIVER(S)          6886.9        COST - ALL FAN UNITS (DOLLARS)         163703.
```

```
                                                                     19 DEC 68     PAGE      1


                                        INPUT VARIABLES FOR FANCST

COST INDEX AS OF JANUARY 1968            272.0          TOTAL FAN CAPACITY (ACFM)          2500000.0
FAN SPEED (RPM)                         1200.0          AIR DENSITY (LBS/FT**3)                 .075
OVERALL EFFICIENCY                        .850          FAN PRESSURE DROP (IN. WATER)           40.0
NUMBER OF FAN UNITS                         1.


                                    FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                       INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)                  2500000.0          WHEEL DIAMETER (INCHES)               104.80
DRIVER BRAKE HORSEPOWER                18470.6          FAN COST (DOLLARS)                    60342.
ACTUAL DRIVER HORSEPOWER               26812.1          MOTOR COST (DOLLARS)                 251577.
FRACTIONAL CAPACITY PER FAN               1.00          EACH FAN UNIT COST (DOLLARS)         311919.

KILOWATTS REQUIRED BY DRIVER(S)        13773.7          COST - ALL FAN UNITS (DOLLARS)       311919.
```

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

31 October 1968

G. D. Schroeder

TECHNICAL MEMORANDUM 004-009-Ch11

DETERMINATION OF THE TOTAL CAPITAL INVESTMENT AND GROSS ANNUAL OPERATING COSTS FOR A GIVEN PROCESS

In making economic studies of sulfur removal processes it is necessary to estimate the gross annual operating cost and the total capital investment. This memorandum describes a method of calculating these figures.

The basis of computing the capital investment cost is the purchase price of the major pieces of equipment. To the purchase price is added amounts of money to account for the erection cost, piping cost, etc. These items are added as a percent of purchase price.

The gross operating cost consists of direct, indirect, and fixed costs. These costs include items such as chemicals and labor, plant overhead, and depreciation and insurance.

The NAPCA has outlined many of the cost procedures to be used in their "General Guide-Lines for the Nine-Area Surveys for SO_2." The procedures used here are consistent with these Guide-Lines.

I. TOTAL CAPITAL INVESTMENT

The purchase price of the equipment must first be given. Several investigators (La-1, Ha-1, Ar-1) have shown how percentages of the purchase price may be applied to cover the cost of erection, instrumentation, etc. The percentage factors given by Lange (La-1) were used in this analysis. These factors are given in Table I.

The basis of selecting the value of the factors of items 2-13 was discussed by Lang (La-1). The working capital, Item 14, is more complex.

For these preliminary cost estimates the working capital will usually be set at 10% of the fixed capital investment. In a detailed cost study working capital would include an analysis of current assets and current liabilities.

A computer program was written to calculate the total capital investment given a purchased equipment cost. An example of the capital cost summary printout sheet is given in Table II.

TABLE I

INSTALLATION COST FACTORS

NO.	ITEM	LANG FACTOR
1.	Purchased Equipment	1.00
2.	Erection Labor	.25
3.	Foundations and Platforms	.18
4.	Piping	.76
5.	Instruments	.15
6.	Insulation	.08
7.	Electrical	.10
8.	Buildings	.25
9.	Land and Yard Improvements	.13
10.	Utilities	.40
11.	Engineering and Construction	.66
12.	Contractor's Fee	.19
13.	Contingency	.59
14.	Working Capital	---

TABLE II

SAMPLE CAPITAL COST ESTIMATE

```
                        SO(2) REMOVAL FROM FLUE GAS

                                CATEGORY
                           DRY METAL OXIDES
                     CAPITAL COST ESTIMATE SUMMARY
                              CASE NO.   1.

           NAME OF PROCESS                          NAME OF EQUIPMENT
          ALKALIZED ALUMINA                           FLUIDIZED BED

      FLUE GAS RATE   83.7 MMSCFM                               MW  800.0

---------------------------------------------------------------------------------

                  ITEM                              COST- THOU. $       $ OF TOTAL
                  ----                              -------------       ----------

   1.  PURCHASED EQUIPMENT                               4171.5            19.18
   2.  ERECTION LABOR                                    1042.9             4.79
   3.  FOUNDATION & PLATFORMS                             750.9             3.45
   4.  PIPING                                            3170.3            14.58
   5.  INSTRUMENTS                                        625.7             2.88
   6.  INSULATION                                         333.7             1.53
   7.  ELECTRICAL                                         417.1             1.92
   8.  BUILDINGS                                         1042.9             4.79
   9.  LAND & YARD IMPROVEMENTS                           542.3             2.49
  10.  UTILITIES                                         1668.6             7.67
  11.        PHYSICAL-PLANT COST                        13765.9            63.29
  12.  ENGINEERING & CONSTRUCTION                        2753.2            12.66

  13.        DIRECT PLANT COST                          16519.1            75.95
  14.  CONTRACTOR-S FEE                                   792.6             3.64
  15.  CONTINGENCY                                       2461.2            11.32

  16.        FIXED CAPITAL COST                         19772.9            90.91
  17.  WORKING CAPITAL                                   1977.3             9.09

             TOTAL INVESTMENT                           21750.2           100.00
  18.  CAPITAL REQUIREMENTS
             $/KW CAPACITY                   27.2
```

II. GROSS ANNUAL OPERATING COST

The gross total yearly operating cost for a given process is the sum of all direct, indirect, and fixed charges (Ar-1). These costs are further defined in Table III.

The direct manufacturing costs are those expenses which are incurred specifically in the manufacture of a product. The specific expenses are discussed below.

1) Raw Materials and Chemicals:

These costs include the purchased cost plus delivery expense of all materials and chemicals consumed in the process. The initial purchase of catalysts should be capatalized and listed in the plant investment. Only catalyst replacement purchases are included as part of the operating cost.

2) Direct Labor:

This consists of the wages paid to employees whose efforts are directed solely toward product manufacture. $6,000/year was used for hourly workers in accordance with preliminary NAPCA Guide-Lines.

3) Supervision:

Supervisory expense is the salaries of all personnel responsible for the direct supervision of productive operations. $7,800/year was used for first-line supervisors and $12,000/year used for area superintendents.

TABLE III

COMPONENTS OF GROSS ANNUAL OPERATING COST

DIRECT COSTS	INDIRECT COSTS	FIXED COSTS
Raw Matl's and Chemicals	Payroll Burden	Depreciation
Direct Labor	Plant Overhead	Taxes
Supervision	Packaging & Shipping	Insurance
Maintenance	Waste Disposal	
Plant Supplies		
Utilities		

4) Maintenance:

Maintenance expenses include the cost of all materials, labor and supervision employed in routine maintenance and repairs. 5% of the fixed capital investment was used for the annual maintenance cost.

5) Plant Supplies:

Plant supplies are gaskets, charts, and lubricants, etc. 15% of the maintenance charges was used for the plant supplies annual cost.

6) Utilities:

Utilities consist of the annual cost of steam, water, electric power, fuel, compressed air, and refrigeration as determined from the process requirements. The following utility unit costs were taken from the NAPCA Guide-Line.

a)	Steam Usage	50¢/thousand pounds	
	Steam Credit	50¢/million pounds	
b)	Electricity	0.006/Kwhr	
c)	Water		
	Raw (untreated)	10¢/M Gal.	(M = 1,000)
	Process (treated)	25¢/M Gal.	
	Cooling Tower	5¢/M Gal.	
d)	Compressed Air	5¢/MCF	

The Indirect Costs are those expenditures which are incurred as a result of, but not directly by, the productive operation. The specific expenses are discussed on the following page.

1) Payroll Burden:

This account covers social security, workmen's compensation, vacations and holidays, life insurance, profit sharing, etc. 20% of the total base labor (Direct Labor + Supervision).

2) Plant Overhead:

Plant overhead is the cost of maintaining service functions such as laboratory, warehousing, medical, engineering, etc. 50% of the sum of direct labor, supervision, maintenance and supplies was used.

3) Packaging and Shipping:

The cost of containers for packaging depends largely upon the chemical and physical nature of the product. Appropriate values will be determined as required.

4) Waste Disposal:

This account is dependent upon each individual process. Appropriate values will be determined as required.

Fixed Costs are those charges reflecting the initial fixed capital investment and associated expenses which remain constant in total with regard to time, regardless of production level.

1) Depreciation:

According to the Internal Revenue Code, depreciation is defined as "a reasonable allowance for exhaustion, wear and tear on property used in the trade or business, including a reasonable allowance for obsolescence." 10%/year of the total fixed capital (except buildings) was used. Buildings were depreciated at 2.22%/yr.

2) Taxes:

Property taxes are completely dependent upon the locality in which the plant is situated. 2% of the fixed capital investment per year was used.

3) Insurance:

1% of the fixed capital investment per year was used.

A computer program was written to calculate the gross annual operating cost. An example of the annual operating cost summary printout sheet is given in Table IV.

Gary D. Schroeder

TABLE IV
SAMPLE OPERATING COST ESTIMATE

```
                    SO(2) REMOVAL FROM FLUE GAS
                             CATEGORY
                         DRY METAL OXIDES

                 OPERATING COST ESTIMATE SUMMARY
               BASIS:  330 DAY/YEAR @   90.0 % CAPACITY

         NAME OF PROCESS                          NAME OF EQUIPMENT
        ALKALIZED ALUMINA                           FLUIDIZED BED

  FLUE GAS RATE    83.7 MMSCFM                                         MW  800.0
                        FIXED CAPITAL COST      19772.9

------------------------------------------------------------------------------------

               ITEM                                COST- THOU. $       % OF TOTAL
               ----                                -------------       ----------

  1.  RAW MATERIALS & CHEMICALS                          1377.9            32.37
  2.  DIRECT LABOR                                         72.3             1.70
  3.  SUPERVISION                                          10.8              .25
  4.  MAINTENANCE, 5% OF FIXED CAPITAL                    988.6            23.23
  5.  SUPPLIES, 15% OF MAINTENANCE                        148.3             3.48
  6.  UTILITIES                                           240.8             5.66
  7.  OTHER                                                  .0              .00
  8.       TOTAL DIRECT COST                             2838.7            66.70
  9.  PAYROLL BURDEN, 20% OF 2 & 3                         16.6              .39
 10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                  610.0            14.33
 11.  PACK & SHIP                                            .0              .00
 12.  WASTE DISPOSAL                                         .0              .00
 13.  OTHER                                                  .0              .00
 14.       TOTAL INDIRECT COST                            626.6            14.72
 15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR              197.7             4.65
 16.  TAXES, 2% OF FIXED CAPITAL                          395.5             9.29
 17.  INSURANCE, 1% OF FIXED CAPITAL                      197.7             4.65
 18.  OTHER                                                  .0              .00
 19.       TOTAL FIXED COST                               790.9            18.58

 20.  TOTAL OPERATING COST                               4256.3           100.00
 21.  COST:  $/TON OF COAL                 1.917
             MIL/KWH                        .672
```

REFERENCES

Ar-1 Aries, R. S., and R. D. Newton: "Chemical Engineering Cost Estimation," McGraw-Hill Book Company, New York, (1955).

Ha-1 Hand, W. E.: "From Flow Sheet to Cost Estimate," Pet. Ref. 37 (9), 331-4, (1958).

La-1 Lang, H. J.: "Simplified Approach to Preliminary Cost Estimation," Chemical Engineering, June, (1948).

TRACOR 6500 TRACOR LANE, AUSTIN, TEXAS 78721

24 June 1969

D. Bond
G. D. Schroeder

TECHNICAL MEMORANDUM OC4-009-Ch26

I. INTRODUCTION

A mass and heat balance (shown in Figure 1) was calculated for the dry metal oxide sulfur oxide removal processes under consideration. Process flow sheets giving the mass balance and heat requirements for the CuO processes for the three plant sizes under consideration are shown in Figures 1, 2 and 3, respectively. The inlet and outlet gas compositions along with plant size for the power plants and smelter gas plant were specified by HEW. These specifications are shown in Table I.

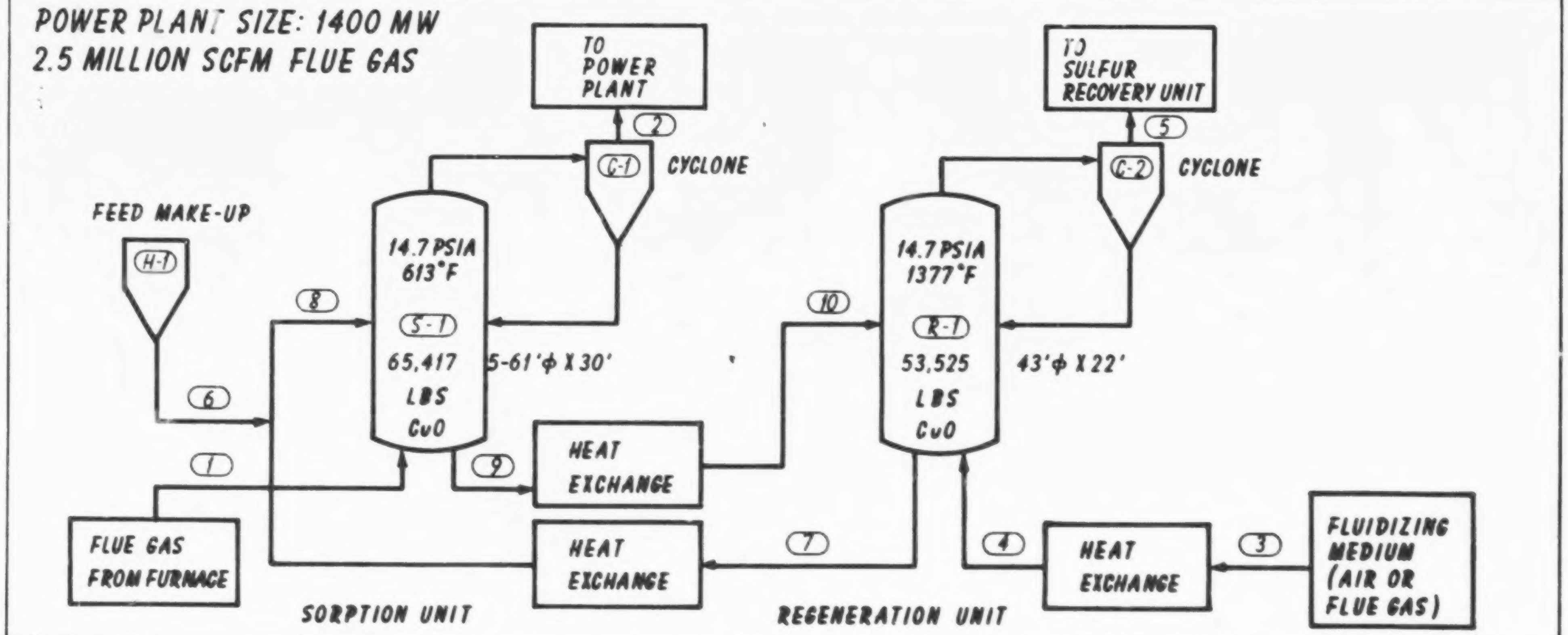
II. MASS BALANCE

The overall mass and component balances were calculated for each unit operation as well as the entire process. The mass balance around the sorber is given by the following equation.

$$G_s(Y_{1s}-Y_{2s})MW_{SO_3} = S(X_1-X_2) \qquad (1)$$

Since G_s (the inlet flow rate to the sorber) and Y_{1s} and Y_{2s} (the mole fractions of SO_3) were specified by HEW, then $S(\Delta X)$ is fixed. Therefore, given sorbent loadings (X_1, X_2) the sorbent circulation rate (S) can be calculated. The sorbent attrition losses were estimated to be .05 percent of the sorbent flow rate for cost calculation.

POWER PLANT SIZE: 1400 MW
2.5 MILLION SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA
613°F
S-1
65,417
LBS
CuO
5-61'φ X 30'
6
1
9
HEAT EXCHANGE
FLUE GAS FROM FURNACE
HEAT EXCHANGE
SORPTION UNIT
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
10
14.7 PSIA
1377°F
R-1
53,525
LBS
CuO
43'φ X 22'
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
REGENERATION UNIT

COMPONENT \ STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	75.86	3.79	0.17	0.17	0.17					
SO_3, MLB/HR	-	-	-	-	90.09					
N_2, MLB/HR	8285.66	8285.66	371.61	371.61	371.61					
CO_2, MLB/HR	2555.39	2555.39	114.61	114.61	114.61					
H_2O, MLB/HR	515.58	515.58	23.12	23.12	23.12					
O_2, MLB/HR	353.99	335.98	15.07	15.07	15.07					
NO, MLB/HR	5.93	5.93	0.26	0.26	0.26					
TOTAL GAS, MLB/HR	11792.41	11702.33	524.84	524.84	614.93					
CuO, MLB/HR						0.12507	240.22	240.22	150.68	150.68
$CuSO_4$, MLB/HR							19.91	19.91	199.54	199.54
TOTAL SOLID, MLB/HR						0.12507	260.13	260.13	350.22	350.22
ENTHALPY, MM BTU/HR	1689.81	1680.44	-	194.43	224.41	-	54.28	20.76	30.14	80.43

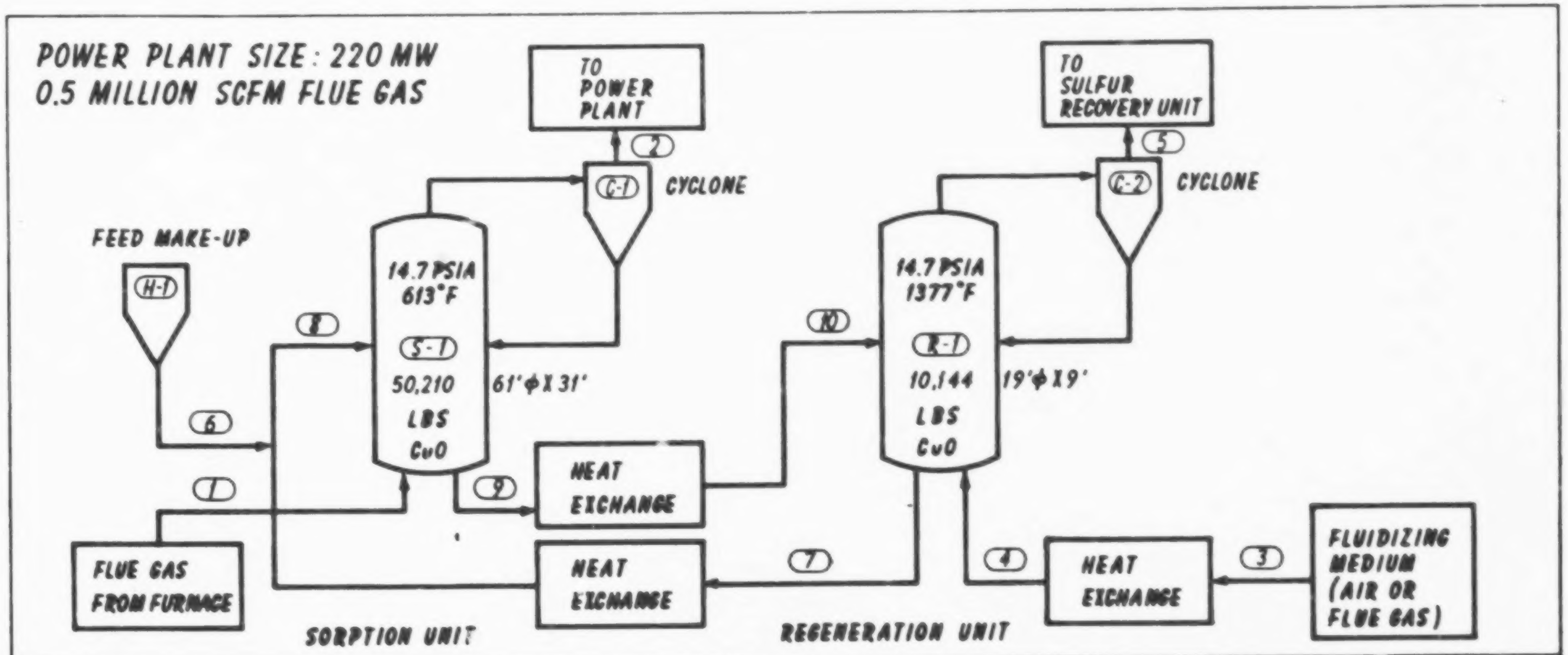
M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

TRACOR
AUSTIN TEXAS

PROCESS FLOWSHEET DATE - JUNE 30, 1969

A6-164-37

Figure 1


POWER PLANT SIZE: 220 MW
0.5 MILLION SCFM FLUE GAS
TO POWER PLANT
②
C-1
CYCLONE
FEED MAKE-UP
H-1
⑧
14.7 PSIA
613°F
S-1
50,210
LBS
CuO
61'φX 31'
⑥
①
⑨
HEAT EXCHANGE
FLUE GAS FROM FURNACE
HEAT EXCHANGE
SORPTION UNIT
TO SULFUR RECOVERY UNIT
⑤
C-2
CYCLONE
⑩
14.7 PSIA
1377°F
R-1
10,144
LBS
CuO
19'φX9'
⑦
④
HEAT EXCHANGE
③
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
REGENERATION UNIT

COMPONENT \ STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	15.17	1.52	0.06	0.06	0.06					
SO_3, MLB/HR	-	-	-	-	17.06					
N_2, MLB/HR	1657.13	1657.13	70.39	70.39	70.39					
CO_2, MLB/HR	511.08	511.08	21.71	21.71	21.71					
H_2O, MLB/HR	103.12	103.12	4.38	4.38	4.38					
O_2, MLB/HR	70.80	67.39	2.86	2.86	2.86					
NO, MLB/HR	1.18	1.18	0.05	0.05	0.05					
TOTAL GAS, MLB/HR	2358.48	2341.42	99.45	99.45	116.51					
CuO, MLB/HR						0.02370	45.51	45.51	37.80	37.80
$CuSO_4$, MLB/HR							3.78	3.78	28.55	28.55
TOTAL SOLID, MLB/HR						0.02370	49.29	49.29	66.35	66.35
ENTHALPY, MM BTU/HR	337.96	336.19	-	35.98	41.50	-	10.04	3.94	5.71	14.87

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

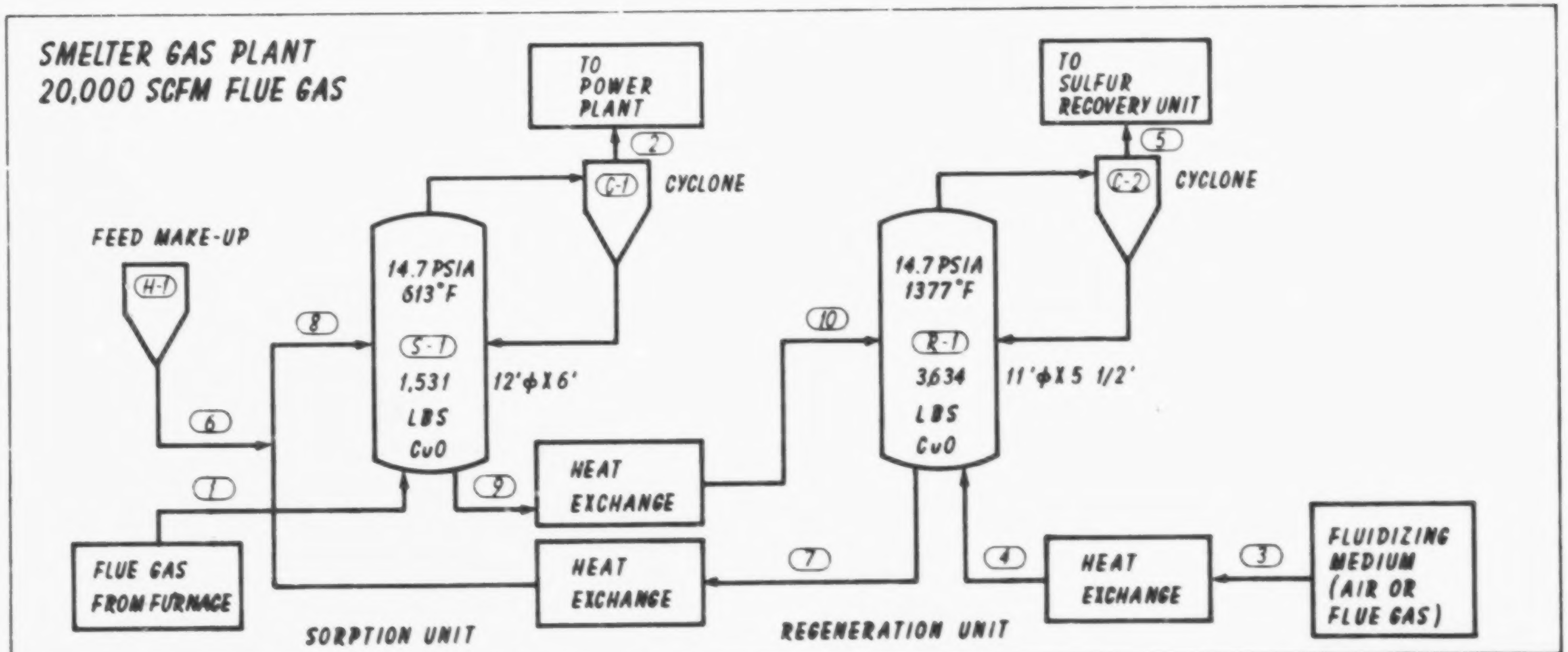
TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET

DATE - JUNE 30, 1969

A6-164-37

Fig 2


SMELTER GAS PLANT
20,000 SCFM FLUE GAS
FEED MAKE-UP
H-1
6
1
8
FLUE GAS FROM FURNACE
14.7 PSIA 613°F
S-1
1,531 LBS CuO
12'φ X 6'
C-1
CYCLONE
2
TO POWER PLANT
9
HEAT EXCHANGE
HEAT EXCHANGE
SORPTION UNIT
10
7
14.7 PSIA 1377°F
R-1
3,634 LBS CuO
11'φ X 5 1/2'
C-2
CYCLONE
5
TO SULFUR RECOVERY UNIT
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
REGENERATION UNIT

COMPONENT \ STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	5.87	0.97	0.38	0.38	0.38					
SO_3, MLB/HR	-	-	-	-	6.12					
N_2, MLB/HR	71.15	71.15	27.97	27.97	27.97					
CO_2, MLB/HR	2.36	2.36	0.93	0.93	0.93					
H_2O, MLB/HR	0.06	0.06	0.02	0.02	0.02					
O_2, MLB/HR	14.46	13.24	5.20	5.20	5.20					
CO, MLB/HR	0.53	0.53	0.21	0.21	0.21					
TOTAL GAS, MLB/HR	94.43	88.31	34.71	34.71	40.83					
CuO, MLB/HR						0.00849	16.30	16.30	10.19	10.19
$CuSO_4$, MLB/HR							1.36	1.36	13.63	13.63
TOTAL SOLID, MLB/HR						0.00849	17.66	17.66	23.82	23.82
ENTHALPY, MM BTU/HR	12.82	12.18	-	12.09	14.12	-	3.69	1.41	2.05	5.47

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

TRACOR
AUSTIN TEXAS

PROCESS FLOWSHEET DATE - JUNE 30, 1969

A6-164-37

Figure 3

TABLE I

Flue Gas Flow Rate	Plant Size	Inlet Flue Gas Concentration Mole Fraction							Outlet SO_2 Concentration
10^6 SCFM	MW	SO_2	N_2	CO_2	H_2O	O_2	NO	CO	Mole Fraction
2.5	1400	0.003	0.749	0.147	0.0725	0.028	0.0005	0	0.00015
0.5	220	0.003	0.749	0.147	0.0725	0.028	0.0005	0	0.00015
0.5	220	0.003	0.749	0.147	0.0725	0.028	0.0005	0	0.0003
.02	Smelter Gas Plant	0.029	0.804	0.017	0.001	0.143	0	0.006	0.005

In order to calculate the amount of fluid (gas) required to operate the regenerator, a mass balance around the regenerator was written.

$$G_r(Y_{2r}-Y_{1r})MW_{SO_3} = S(X_1-X_2) \qquad (2)$$

By assuming that the inlet SO_3 concentration (Y_{1r}) is equal to zero and by setting the outlet SO_3 concentration (Y_{2r}) equal to 6 percent (required to operate a contact sulfuric acid plant) the gas flow rate (G_r) to the regenerator can be calculated. From G_r the regenerator can be sized. Knowing the regenerator size, the capital cost can be calculated from the vessel dimensions.

III. HEAT BALANCE

Using kinetic data obtained from TGA measurements, the temperatures of operation of the sorber and regenerator were determined for each dry metal oxide. To simplify preliminary calculations, an average temperature for the sorber and regenerator (assuming no heat gradient in the fluidized bed) was used in making heat transfer computations.

The enthalpies of the streams were calculated using 60°F (289°K) as the base temperature from Equations 3 and 4.

$$(\Delta H_T)_j = \sum_i^{n_j} Mi \int_{T_1}^{T} C_{Pi}\, dT = \sum_i^{n_j} Mi \int_{T_1}^{T} (A_i + B_i T)dT \qquad (3)$$

$$(\Delta H_T)_j = \sum_i^{n_j} Mi \left[A_i(T-289) + \frac{B_i}{2}(T^2-289^2)\right]$$

$$= \sum_i^{n_j} Mi(\Delta H_T)_i \qquad (4)$$

where j = number of the stream under consideration

i = component under consideration

n_j = number of components in stream j

The heat capacities were taken from the TRACOR data base and the heat of reaction was calculated by the computer program AIRPOL.

The heat requirement of the gaseous-solid stream between the sorber and the regenerator was found by taking the difference between the heat content of the outlet and inlet streams of the sorber and regenerator. The available enthalpy from the solid on recycle from the regenerator to the sorber was found similarly. Heat losses to the atmosphere through insulated vessels were approximated for both the sorber and regenerator.

The net overall heat requirement for the process plant is equal to the net available enthalpy from the sorber subtracted from the net heat requirement of the regenerator.

Net Heat for Plant = Heat Requirement of Regenerator
- Heat Available from Sorber

The net heat requirement (evaluated at 50¢/million BTU) was part of the total operating cost for the process.

NOMENCLATURE

A_i, B_i	coefficients for heat capacity equation of component i, requiring temperature in degrees Kelvin
C_{pi}	heat capacity of component i, cals/(g mole^{o}K)
G_r	gas feed rate to regenerator, lb. mole/hr.
G_s	gas feed rate to sorber, lb. mole/hr.
$(\Delta H_T)_i$	enthalpy of component i at temperature T, BTU/hr.
$(\Delta H_T)_j$	enthalpy of stream j at temperature T, BTU/hr.
Mi	molar flow rate of component i, lb. mole/hr.
MW_{SO_3}	molecular weight of SO_3, lb./lb. mole
n_j	number of components in stream j
S	sorbent circulation rate, lb./hr.
T	temperature of stream, ^{o}K
T_1	chosen base temperature, 289^{o}K(60^{o}F)
X_1	weight ratio of SO_3 carried by sorbent leaving sorber, lb. SO_3/lb. sorbent
X_2	weight ratio of SO_3 carried by sorbent entering sorber, lb. SO_3/lb. sorbent
Y_{1r}	mole fraction SO_3 entering regenerator, (lb. mole SO_2/hr.)/(lb. mole gas/hr.)
Y_{2r}	mole fraction SO_3 leaving regenerator, (lb. mole SO_2/hr.)/(lb. mole gas/hr.)
Y_{1s}	mole fraction SO_3 entering sorber, (lb. mole SO_2/hr.)/(lb. mole gas/hr.)
Y_{2s}	mole fraction SO_3 leaving sorber, (lb. mole SO_2/hr.)/(lb. mole gas/hr.)

8.2 THERMODYNAMIC, KINETIC, AND ECONOMIC DATA

8.2.1 Data Base of Thermodynamic Properties

TABLE OF CONTENTS
CHEMICAL COMPOUND DATA FILE

```
   AG              2 AS2(CO3)3         BI                  CAWO4
   AGVO3           2 AS2(SO3)3         BI2O3               CA(OH)2
   AG2AL2O4        2 AS2(SO4)3         BI2S3               CA2FE2O5
   AG2CO3            B                 BI2(AL2O4)3         CD
   AG2CRO4           BA                BI2(CO3)3           CDAL2O4
   AG2CR2O4          BAAL2O4           BI2(CRO4)3          CDCO3
   AG2FE2O4          BACO3             BI2(CR2O4)3         CDCRO4
   AG2MOO4           BACRO4            BI2(FE2O4)3         CDCR2O4
   AG2O              BACR2O4           BI2(MOO4)3          CDFE2O4
   AG2S              BAFE2O4           BI2(SO3)3           CDMOO4
   AG2SO3          2 BAMOO3            BI2(SO4)3           CDO
   AG2SO4            BAMOO4            BI2(TIO3)3          CDS
   AG2TIO3           BAO               BI2(V2O6)3          CDSO3
   AG2WO4            BAS               BI2(WO4)3           CDSO4
   AL                BASO3           2 BO(GAS)             CDTIO3
   AL2O3             BASO4             BS(GAS)             CDV2O6
 2 AL2S              BATIO3            B2O3                CDWO4
   AL2S3             BAV2O6            B2S3                CE
   AL2TIO5           BAWO4             C                   CEO2
   AL2(CO3)3       2 BA2TIO4           CA                2 CES
   AL2(CRO4)3        BE                CAAL2O4             CES2
   AL2(CR2O4)3       BEAL2O4         2 CAAL4O7           2 CE(CO3)2
   AL2(FE2O4)3       BECO3             CACO3             2 CE(SO3)2
   AL2(MOO4)3        BECRO4            CACRO4              CE(SO4)2
   AL2(SO3)3         BECR2O4           CACR2O4             CE2O3
   AL2(SO4)3         BEFE2O4           CAFE2O4             CE2S3
   AL2(TIO3)3        BEMOO4          2 CAMOO3            2 CE2(CO3)3
   AL2(V2O6)3        BEO               CAMOO4            2 CE2(SO3)3
   AL2(WO4)3         BES               CAO                 CE2(SO4)3
   AS                BESO3             CAS               2 CE3S4
   AS2O3             BESO4             CASO3               CO
 2 AS2O5             BETIO3            CASO4               COAL2O4
   AS2S3             BEV2O6            CATIO3              COCO3
 2 AS2S5             BEWO4             CAV2O6              COCRO4

                   1 INDICATES ADDITION OR REVISION
                   2 INDICATES INCOMPLETE DATA
```

TABLE OF CONTENTS
CHEMICAL COMPOUND DATA FILE

```
  COCR2O4           CUCR2O4             FESO4               HF
  COFE2O4           CUFEO2              FESO2               HFO2
  COMOO4            CUFE2O4             FETIO3            2 HFS2
2 COMPOUND          CUMOO4              FEV2O6            2 HF(CO3)2
  COO               CUO                 FEWO4             2 HF(SO3)2
  COS               CUO•CUSO4           FE2O3             2 HF(SO4)2
  COSO3             CUS               2 FE2TIO4             H2
  COSO4             CUSO3             2 FE2TIO5             H2O(GAS)
  COTIO3            CUSO4               FE2(AL2O4)3         IR
  COV2O6            CUTIO3              FE2(CO3)3           IRO2
  COWO4             CUVO3               FE2(CRO4)3          IRS2
  CO2               CUV2O6              FE2(CR2O4)3       2 IRS3
2 CO2S3             CUWO4               FE2(MOO4)3        2 IR(SO4)2
  CO3O4             CU2AL2O4            FE2(SO3)3         2 IR2S3
2 CO3S4             CU2CO3              FE2(SO4)3           K
  CR                CU2CRO4             FE2(TIO3)3          KALO2
  CRO3              CU2CR2O4            FE2(V2O6)3          KFEO2
  CR2O3             CU2MOO4             FE2(WO4)3           KVO3
2 CR2O7             CU2O                FE3O4               K2CO3
2 CR2S3             CU2S                GA                  K2CRO4
2 CR2(CO3)3         CU2SO3            2 GAS                 K2CR2O4
2 CR2(SO3)3         CU2SO4              GA2O3               K2MOO4
2 CR2(SO4)3         CU2TIO3             GA2S3               K2O
  CS                CU2WO4            2 GA2(CO3)3           K2S
2 CS2CO3            C(O)              2 GA2(SO3)3           K2SO3
2 CS2O              FE                2 GA2(SO4)3           K2SO4
2 CS2S              FEAL2O4             GE                  K2TIO3
2 CS2SO3            FECO3             2 GEO(GAS)            K2WO4
  CS2SO4            FECRO4              GEO2                LA
  CS2(G)            FECR2O4             GES               2 LAS
  CU                FEMOO4            2 GES2              2 LAS2
  CUAL2O4           FEO               2 GE(CO3)2            LA2O3
  CUCO3             FES               2 GE(SO3)2            LA2S3
  CUCRO4            FESO3             2 GE(SO4)2          2 LA2(CO3)3

                    1 INDICATES ADDITION OR REVISION
                    2 INDICATES INCOMPLETE DATA
```

```
                               TABLE OF CONTENTS
                          CHEMICAL COMPOUND DATA FILE

  2 LA2(SO3)3         MNCO3            2 MO(SO3)3           NIFE2O4
    LA2(SO4)3         MNCRO4           2 MO(SO4)3           NIMOO4
    LI                MNCR2O4          2 MO2S3              NIO
    LIALO2            MNFE2O4            NA               1 NIS
    LIFEO2            MNMOO4             NAALO2             NISO3
    LIVO3             MNO                NAFEO2             NISO4
    LI2CO3            MNO2               NAVO3              NITIO3
    LI2CRO4           MNS                NA2CO3             NIV2O6
    LI2CR2O4          MNSO3              NA2CRO4            NIWO4
    LI2MOO4           MNSO4              NA2CR2O4           NI3S2
    LI2O              MNS2               NA2MOO4            NO
    LI2S              MNTIO3             NA2MO2O7           NO2
    LI2SO3            MNV2O6             NA2O               N2O4
    LI2SO4            MNWO4              NA2S               N2(GAS)
    LI2TIO3         2 MN(SO4)2           NA2SO3             O2
    LI2WO4            MN2O3              NA2SO4             PB
    MG                MN2(AL2O4)3        NA2TIO3            PBAL2O4
    MGAL2O4           MN2(CO3)3        2 NA2TI2O5           PBCO3
    MGCO3             MN2(CRO4)3       2 NA2TI3O7         2 PBCO3*PBO
    MGCRO4            MN2(CR2O4)3        NA2WO4           2 PBCO3*2PBO
    MGCR2O4           MN2(FE2O4)3        NA2W2O7            PBCRO4
    MGFE2O4           MN2(MOO4)3         NB                 PBCR2O4
    MGMOO4            MN2(SO3)3        2 NBO                PBFE2O4
    MGO               MN2(SO4)3        2 NBO2               PBMOO4
    MGS               MN2(TIO3)3         NB2O5              PBO
    MGSO3             MN2(V2O6)3       2 NB2S5              PBO*PBSO4
    MGSO4             MN2(WO4)3        2 NB2(CO3)5          PBO2
    MGTIO3            MN3O4            2 NB2(SO3)5          PBS
    MGTI2O5           MO               2 NB2(SO4)5          PBSO3
    MGV2O6          2 MOO2               NI                 PBSO4
    MGWO4             MOO3               NIAL2O4            PBTIO3
  2 MG2TIO4           MOS2               NICO3              PBV2O6
    MN                MOS3               NICRO4             PBWO4
    MNAL2O4         2 MO(CO3)3           NICR2O4          2 PB(SO4)2

                   1 INDICATES ADDITION OR REVISION
                   2 INDICATES INCOMPLETE DATA
```

TABLE OF CONTENTS
CHEMICAL COMPOUND DATA FILE

2 PB3O4
PD
2 PDCO3
PDO
PDS
2 PDSO3
2 PDSO4
2 PDS2
RB2CO3
2 RB2O
2 RB2S
2 RB2SO3
RB2SO4
RE
2 REO2
2 REO3
2 RES2
2 RES3
2 RE2O7
2 RE2O8
2 RE2S7
RH
2 RHCO3
RHO
2 RHS
2 RHSO3
2 RHSO4
RH2O
RH2O3
2 RH2S
2 RH2SO4
2 RH2S3
2 RH2(SO4)3
RU
2 RUO2
2 RUO3(GAS)
2 RUO4(GAS)
2 RUS2
S
SB
SB2O3
SB2O4
2 SB2O5
SB2S3
SB2(AL2O4)3
SB2(CO3)3
SB2(CRO4)3
SB2(CR2O4)3
SB2(FE2O4)3
SB2(MOO4)3
SB2(SO3)3
SB2(SO4)3
SB2(TIO3)3
SB2(V2O6)3
SB2(WO4)3
SC
SC2O3
2 SC2(CO3)3
2 SC2(SO3)3
2 SC2(SO4)3
SI
2 SIO(GAS)
SIO2
SIS(GAS)
SIS2
2 SI(CO3)2
2 SI(SO3)2
2 SI(SO4)2
SN
2 SNCO3
SNO
SNO2
SNS
2 SNSO3
2 SNSO4
SNS2
SN(AL2O4)2
SN(CO3)2
SN(CRO4)2
SN(CR2O4)2
SN(FE2O4)2
SN(MOO4)2
SN(SO3)2
SN(SO4)2
SN(TIO3)2
SN(V2O6)2
SN(WO4)2
SO2
SO3
SR
SRAL2O4
SRCO3
SRCRO4
SRCR2O4
SRFE2O4
2 SRMOO3
SRMOO4
SRO
SRS
SRSO3
SRSO4
SRTIO3
SRV2O6
SRWO4
2 SR2TIO4
S(GAS)
TA
TA2O5
2 TA2S5
2 TA2(CO3)5
2 TA2(SO3)5
2 TA2(SO4)5
TH
THO2
2 THS
THS2
TH(AL2O4)2
TH(CO3)2
TH(CRO4)2
TH(CR2O4)2
TH(FE2O4)2
TH(MOO4)2
TH(SO3)2
TH(SO4)2
TH(TIO3)2
TH(V2O6)2
TH(WO4)2
TH2S3
TI
2 TICO3
TIO
TIO2
2 TISO3
2 TISO4
TIS2
2 TI(SO4)

1 INDICATES ADDITION OR REVISION
2 INDICATES INCOMPLETE DATA

TABLE OF CONTENTS
CHEMICAL COMPOUND DATA FILE

TI2O3
2 TI2(CO3)3
2 TI2(SO3)3
2 TI2(SO4)3
TI3O5
U
UO2
UO2SO4
UO3
2 US
US2
U(AL2O4)2
U(CO3)2
U(CRO4)2
U(CR2O4)2
U(FE2O4)2
U(MOO4)2
U(SO3)2
U(SO4)2
U(TIO3)2
U(V2O6)2
U(WO4)2
2 U2S3
U3O8
V
2 VCO3
VO
VOSO4
VS
2 VSO3
2 VSO4
V2O3
V2O4
V2O5
2 V2S3
2 V2S4
2 V2S5
2 V2(CO3)3
2 V2(SO3)3
2 V2(SO4)3
W
WO2
WO3
WS2
2 W(CO3)2
2 W(CO3)3
2 W(SO3)2
2 W(SO3)3
2 W(SO4)2
2 W(SO4)3
Y
Y2O3
2 Y2(CO3)3
2 Y2(SO3)3
2 Y2(SO4)3
ZN
ZNAL2O4
ZNCO3
ZNCRO4
ZNCR2O4
ZNFE2O4
ZNMOO4
ZNO
ZNO*2ZNSO4
ZNS
ZNSO3
ZNSO4
ZNTIO3
ZNV2O6
ZNWO4
ZN2TIO4
ZR
ZRO2
2 ZRS2
ZR(AL2O4)2
ZR(CO3)2
ZR(CRO4)2
ZR(CR2O4)2
ZR(FE2O4)2
ZR(MOO4)2
ZR(SO3)2
ZR(SO4)2
ZR(TIO3)2
ZR(V2O6)2
ZR(WO4)2

1 INDICATES ADDITION OR REVISION
2 INDICATES INCOMPLETE DATA

HEAT OF FORMATION, ENTROPY, AND TRANSITION DATA

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TYPE	REFERENCES
AG	.00		10.20	LA-001	961.28	2.69	S-L	LA-001
AGVO3	-199.53	TR-002	32.60	KE-001				
AG2AL2O4	-413.64	TR-002	44.20	TR-003				
AG2CO3	-120.88	LA-001	39.97	LA-001				
AG2CRO4	-172.37	CA-058	52.00	CA-058				
AG2CR2O4	-308.20	TR-002	49.60	KE-001				
AG2FE2O4	-205.53	TR-002	51.26	TR-003				
AG2MOO4	-216.60	CA-058	61.86	CA-058				
AG2O	-7.30	LA-001	29.07	LA-001				
AG2S	-7.75	LA-001,NB-003	34.00	LA-001,KU-001	179.00	1.05	S-S	LA-001
					582.00		S-S	
					842.00	3.36	S-L	
AG2SO3	-114.40	CA-006	44.60	TR-003				
AG2SO4	-170.36	LA-001	47.76	LA-001	441.00	4.46	S-S	LA-001,CA-002
					657.00	4.28	S-L	
AG2TIO3	-239.37	TR-002	40.10	TR-003				
AG2WO4	-230.70	HE-001	27.16	CA-058				
AL	.00		6.76	LA-001	658.60	2.56	S-L	LA-001
AL2O3	-400.16	LA-001,NB-002	12.17	LA-001,NB-002	975.00	20.59	S-S	LA-001
					2045.00	26.04	S-L	
					3530.00		L-G	
AL2S	-29.38	LA-001	73.10	LA-001				
AL2S3	-172.85	LA-001,TR-010	23.00	LA-001,NB-003	1100.00		S-L	LA-001
AL2TIO5	-622.96	CA-043	26.20	KU-001	1890.00		S-L	KU-001
AL2(CO3)3	-707.03	TR-002	40.00	TR-003				
AL2(CRO4)3	-849.81	TR-002	78.60	KE-001				
AL2(CR2O4)3	-1238.00	TR-002	68.40	KE-001				
AL2(FE2O4)3	-975.13	TR-002	78.60	KE-001				
AL2(MOO4)3	-979.92	TR-002	64.60	TR-007				
AL2(SO3)3	-661.91	TR-002	49.00	TR-003				
AL2(SO4)3	-820.38	LA-001,NB-003	57.14	LA-001,NB-003				
AL2(TIO3)3	-1074.60	TR-002	42.60	KE-001				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
AL2(V206)3	-1532.00	TR-002	115.20	KE-001				
AL2(WO4)3	-1023.70	TR-002	62.20	TR-007				
AS	.00		8.39	LA-001				
AS203	-156.91	LA-001,KU-001	25.59	LA-001,KU-001	274.00	11.90	S-S	
					315.00	4.47	S-S	
AS205	-219.31	LA-001	25.18	LA-001				
AS2S3	-30.00	KU-001,TR-010	27.71	TR-003	170.00		S-S	
					300.00		S-L	
AS2S5	-35.00	KU-001	44.20	KE-001	170.00		S-S	KU-001
					300.00		S-L	
AS2(CO3)3			46.90	TR-003				
AS2(SO3)3			55.90	TR-003				
AS2(SO4)3			64.00	TR-003				
B	.00		1.40	LA-001	2030.00	5.30	S-L	LA-001
BA	.00		15.49	LA-001	370.00	.14	S-S	LA-001
					710.00	1.83	S-L	
BAAL204	-566.67	TR-002	28.58	TR-003				
BACO3	-287.16	LA-001	26.78	LA-001	806.00	3.87	S-S	LA-001
					968.00	.69	S-S	
BACRO4	-336.37	TR-002	38.15	TR-003				
BACR204	-516.32	TR-002	33.22	TR-003				
BAFE204	-350.49	CA-061	35.37	TR-003				
BAMOO3	-308.70	CA-024						
BAMOO4	-377.04	TR-002	33.97	TR-003				
BAO	-132.07	LA-001,CA-007	16.79	LA-001	1923.00	13.78	S-L	LA-001
					2700.00		L-G	
BAS	-106.00	CA-019,TR-010	20.90	LA-001,TR-010				
BASO3	-282.60	NB-003	28.60	TR-003				
BASO4	-349.99	LA-001	31.49	LA-001	1150.00		S-S	LA-001,CA-002
					1350.00	9.70	S-L	
BATIO3	-394.60	CA-063,TR-002	25.78	LA-001				
BAV206	-567.34	TR-002	45.78	TR-003				
BAWO4	-406.00	CA-025	32.00	CA-025				
BA2TIO4			47.00	KU-001				

```
   COMPOUND          HEAT  OF    REFERENCES       ABSOLUTE    REFERENCES                      TRANSITION DATA
                     FORMATION                    ENTROPY                      TEMP.    HEAT   TYPE   REFERENCES
                     25 DEG.C                     CAL/GMOLE/                   DEG.C    KCAL/
                     KCAL/GMOLE                     DEG. K                              GMOLE


BE                          .00                       2.27    LA-001           1283.00     2.99  S-L  LA-001
BEAL204                 -542.99  TR-002,CA-065       19.18    TR-003
BECO3                   -246.89  TR-002              15.69    TR-003
BECRO4                  -294.44  TR-002              28.75    TR-003
BECR204                 -424.43  TR-002              23.82    TR-003
BEFE204                 -335.85  TR-002              25.97    TR-003
BEMOO4                  -337.96  TR-002              24.57    TR-003
BEO                     -143.03  LA-001               3.37    LA-001           2550.00    16.99  S-L  LA-001
                                                                               4120.00           L-G
BES                      -55.90  KU-001,NB-003        8.40    KU-001,LA-001
BESO3                   -232.20  TR-002              19.20    TR-003
BESO4                   -285.65  NB-003              18.62    CA-005            880.00     3.30  S-S  CA-005
BETIO3                  -368.42  TR-002              17.21    TR-003
BEV206                  -521.71  TR-002              36.38    TR-003
BEWO4                   -352.45  TR-002              23.56    TR-003
BI                          .00                      13.56    LA-001            271.30     2.60  S-L  LA-001
BI203                   -138.08  LA-001,NB-001       36.12    LA-001,NB-001     704.00           S-S  LA-001
                                                                                817.00     6.81  S-L
BI2S3                    -43.80  NB-003,WI-001       35.30    NB-003
BI2(AL204)3            -1349.30  TR-002              78.20    KE-001
BI2(CO3)3               -476.57  TR-002              55.20    TR-003
BI2(CRO4)3              -618.62  TR-002             106.40    KE-001
BI2(CR204)3            -1024.00  TR-002              96.20    KE-001
BI2(FE204)3             -727.92  TR-002             106.40    KE-001
BI2(MOO4)3              -749.96  TR-002              79.80    TR-007
BI2(SO3)3               -437.28  TR-002              64.20    TR-003
BI2(SO4)3               -608.10  NB-001,WI-001       72.30    TR-003
BI2(TIO3)3              -826.08  TR-002              70.40    KE-001
BI2(V206)3             -1300.00  TR-002             143.00    KE-001
BI2(WO4)3               -794.59  TR-002              77.40    TR-007
BO(GAS)                   -5.30  LA-001              48.59    LA-001
BS(GAS)                  -80.00  JA-001              51.65    JA-001
B203                    -306.10  KU-001,TR-010       12.86    LA-001            450.00     5.49  S-L  LA-001
B2S3                     -57.00  LA-001,NB-003       14.61    TR-003            310.00           S-L  LA-001,KU-001
```

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
C	.00	JA-001	1.36	JA-001				
CA	.00		9.94	LA-001	440.00	.24	S-S	LA-001
					850.00	2.07	S-L	
CAAL2O4	-555.50	KU-001	27.30	KU-001				
CAAL4O7			42.50	KU-001				
CACO3	-288.11	LA-001	22.19	LA-001				
CACRO4	-329.44	LA-001	32.01	LA-001				
CACR2O4	-492.40	CA-038	28.82	TR-003				
CAFE2O4	-367.25	CA-042,TR-010	34.70	KU-001,LA-001	1240.00	25.85	S-L	KU-001
CAMOO3	-277.80	CA-020	24.70	CA-021				
CAMOO4	-369.21	CA-077,TR-010	29.30	KU-001,CA-017				
CAO	-151.73	LA-001,NB-003	9.48	NB-003,LA-001	2603.00	12.23	S-L	LA-001
					3570.00		L-G	
CAS	-114.20	LA-001,TR-010	13.50	KU-001,NB-003				
CASO3	-275.88	MA-001	24.20	LA-001				
CASO4	-340.19	LA-001	25.49	LA-001	1193.00		S-S	LA-001,CA-002
					1397.00	6.69	S-L	
CATIO3	-370.00	CA-053	22.40	KU-001,TR-010	1260.00	.55	S-S	KU-001,LA-001
CAV2O6	-558.70	CA-050	42.80	CA-052				
CAWO4	-402.50	CA-077,TR-010	30.20	KU-001,TR-010				
CA(OH)2	-235.60	LA-001	19.92	LA-001				
CA2FE2O5	-507.28	KU-001	45.10	KU-001				
CD	.00		12.37	LA-001	321.00	1.53	S-L	LA-001
CDAL2O4	-466.54	TR-002	27.78	TR-003				
CDCO3	-178.46	LA-001	25.18	LA-001				
CDCRO4	-224.10	TR-002	37.35	TR-003				
CDCR2O4	-361.66	TR-002	32.42	TR-003				
CDFE2O4	-258.73	TR-002	34.57	TR-003				
CDMOO4	-267.85	TR-002	33.17	TR-003				
CDO	-61.18	LA-001	13.09	LA-001				
CDS	-34.47	LA-001,NB-003	16.96	LA-001,NB-003				
CDSO3	-163.90	CA-001	27.80	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TYPE	REFERENCES
CDSO4	-221.20	LA-001	29.41	LA-001	792.00	1.49	S-S	LA-001,CA-002
					859.00	2.39	S-S	
					1000.00		S-L	
CDTIO3	-292.23	TR-002	25.80	TR-003				
CDV2O6	-451.32	TR-002	44.98	TR-003				
CDWO4	-283.05	TR-002,WI-001	32.16	TR-003				
CE	.00		16.63	LA-001	393.00		S-S	LA-001
					440.00		S-S	
					777.00	3.08	S-L	
CEO2	-233.00	LA-001,NB-003	14.89	CA-066				
CES	-118.00	KU-001	18.80	TR-003				
CES2	-153.90	NB-003	18.82	TR-003				
CE(CO3)2	-468.01	TR-002						
CE(SO3)2	-443.14	TR-002						
CE(SO4)2	-560.00	NB-003,WI-001	37.80	TR-003				
CE2O3	-434.90	KU-001,CA-018	36.00	CA-014,TR-010				
CE2S3	-298.70	NB-003,KU-001	32.41	TR-003	1890.00		S-L	KU-001
CE2(CO3)3			51.60	TR-003				
CE2(SO3)3			60.60	TR-003				
CE2(SO4)3	-953.00	MA-001	68.70	TR-003				
CE3S4	-421.50	KU-001			2050.00		S-L	KU-001
CO	.00		7.18	LA-001	445.00	.00	S-S	LA-001
					1127.00	.13	S-S	
					1490.00	3.66	S-L	
COAL2O4	-466.50	CA-055	25.48	TR-003				
COCO3	-173.30	KE-002	21.99	TR-003				
COCRO4	-221.49	TR-002	35.05	TR-003				
COCR2O4	-350.60	CA-034	27.00	CA-034				
COFE2O4	-255.26	TR-002	32.20	KU-001,TR-003	500.00		S-S	CA-056
COMOO4	-265.21	TR-002	30.87	TR-003				
COMPOUND	.00							
COO	-57.07	LA-001	12.65	LA-001	1800.00	9.60	S-L	LA-001
COS	-21.07	RO-004,TR-010	15.82	TR-003	1100.00		S-L	LA-001
COSO3	-161.75	TR-002	25.50	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
COSO4	-211.90	AD-001,TR-010	27.07	LA-001	691.00	.51	S-S	CA-002
COTIO3	-289.50	CA-033,CA-055	23.80	CA-033				
COV2O6	-448.77	TR-002	42.68	TR-003				
COWO4	-280.61	TR-002	29.86	TR-003				
CO2	-94.01	LA-001	51.03	LA-001				
CO2S3	-51.00	NB-003	26.40	TR-003				
CO3O4	-216.20	LA-001	24.61	LA-001				
CO3S4	-75.00	KU-001						
CR	.00		5.68	LA-001	1840.00	.35	S-S	LA-001
					1903.00	3.49	S-L	
CRO3	-142.03	LA-001	17.20	LA-001	187.00		S-L	
CR2O3	-272.58	LA-001	19.37	LA-001	37.80		S-S	LA-001
					2440.00		S-L	
CR2O7	-344.97	LA-001	70.48	LA-001				
CR2S3			25.21	TR-003				
CR2(CO3)3			44.40	TR-003				
CR2(SO3)3			53.40	TR-003				
CR2(SO4)3			61.50	TR-003				
CS	.00		20.14	LA-001	28.64	.52	S-L	LA-001
CS2CO3	-272.57	TR-002	43.23	TR-003	792.00		S-L	RE-001
CS2O	76.00	LA-001,CO-001	29.90	TR-003,CO-001	490.00		S-L	
CS2S	-81.10	NB-003,KU-001	35.14	TR-003				
CS2SO3	-263.60	CA-080	46.20	TR-003				
CS2SO4	.00	LA-001	50.89	TR-003	660.00		S-S	LA-001,CA-002
					722.00	.50	S-S	
					1004.00	9.58	S-L	
CS2(G)	27.55	LA-001	56.81	LA-001				
CU	.00		7.96	LA-001	1084.00	3.11	S-L	LA-001
CUAL2O4	-439.03	TR-002	25.68	TR-003				
CUCO3	-142.10	LA-001	21.02	LA-001				
CUCRO4	-189.80	TR-002	35.25	TR-003				
CUCR2O4	-321.74	TR-002	30.32	TR-003				
CUFEO2	-115.90	TR-002	21.20	CA-062	1197.00	15.38	S-L	CA-062
CUFE2O4	-237.51	CA-042	32.47	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
CUMOO4	-233.21	TR-002	31.07	TR-003				
CUO	-39.49	LA-001	10.19	LA-001				
CUO•CUSO4	-222.35	IN-001	38.03	IN-001				
CUS	-11.50	LA-001,KU-001	15.90	LA-001,KU-001				
CUSO3	-127.28	TR-002	25.70	TR-003				
CUSO4	-184.22	LA-001	27.07	LA-001				
CUTIO3	-264.49	TR-002	23.71	TR-003				
CUVO3	-200.68	TR-002	29.60	KE-001				
CUV2O6	-417.15	TR-002	42.88	TR-003				
CUWO4	-247.76	TR-002,WI-001	30.06	TR-003				
CU2AL2O4	-439.71	TR-002	40.20	TR-003				
CU2CO3	-142.29	TR-002	37.63	TR-003				
CU2CRO4	-189.90	TR-002	47.00	KE-001				
CU2CR2O4	-319.04	TR-002	43.60	KE-001				
CU2MOO4	-233.18	TR-002	46.75	TR-007				
CU2O	-40.78	LA-001	22.52	LA-001	1230.00	13.38	S-L	LA-001
CU2S	-19.93	LA-001,NB-003	28.88	LA-001,NB-003	103.00	1.34	S-S	LA-001,KU-001
					350.00	.20	S-S	
					1127.00	5.49	S-L	
CU2SO3	-127.06	TR-002	40.60	TR-003				
CU2SO4	-179.51	LA-001	38.46	LA-001				
CU2TIO3	-265.20	TR-002	36.10	TR-003				
CU2WO4	-247.85	TR-002	45.70	TR-007				
C(O)	-26.40	LA-001	47.16	LA-001				
FE	.00		6.49	LA-001	760.00	.00	S-S	LA-001
					906.00	.21	S-S	
					1401.00	.11	S-S	
					1535.00	3.70	S-L	
FEAL2O4	-474.40	CA-032,CA-054	25.40	KU-001				
FECO3	-178.55	LA-001	22.19	LA-001				
FECRO4	-225.69	TR-002	34.85	TR-003				
FECR2O4	-349.50	CA-068,TR-010	34.90	LA-001,KU-001	2180.00		S-L	LA-001,KU-001
FEMOO4	-269.45	TR-002	30.90	CA-064				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
FEO	-63.76	LA-001	14.19	LA-001	-84.70		S-S	LA-001
					1377.00	7.48	S-L	
FES	-22.80	KU-001,LA-001	15.20	KU-001,LA-001	138.00	.57	S-S	KU-001,LA-001
					325.00	.12	S-S	
					1195.00	7.73	S-L	
FESO3	-165.54	TR-002	25.30	TR-003				
FESO4	-220.41	LA-001	25.68	LA-001				
FES2	-42.45	LA-001,KU-001	12.70	LA-001,KU-001				
FETIO3	-295.10	LA-001,TR-010	25.30	LA-001,KU-001	1370.00	21.70	S-L	LA-001,KU-001
FEV2O6	-452.87	TR-002	42.48	TR-003				
FEWO4	-284.52	TR-002	31.50	CA-064				
FE2O3	-196.42	LA-001	20.88	LA-001	677.00	.16	S-S	LA-001
					767.00		S-S	
FE2TIO4			39.00	KU-001				
FE2TIO5			37.40	KU-001				
FE2(AL2O4)3	-1349.30	TR-002	61.60	KE-001				
FE2(CO3)3	-502.66	TR-002	44.80	TR-003				
FE2(CRO4)3	-645.46	TR-002	89.80	KE-001				
FE2(CR2O4)3	-1033.40	TR-002	79.60	KE-001				
FE2(MOO4)3	-775.50	TR-002	69.40	TR-007				
FE2(SO3)3	-457.40	TR-002	53.80	TR-003				
FE2(SO4)3	-615.60	CA-009	61.90	TR-003				
FE2(TIO3)3	-870.56	TR-002	53.80	KE-001				
FE2(V2O6)3	-1327.70	TR-002	126.40	KE-001				
FE2(WO4)3	-817.32	TR-002	67.00	TR-007				
FE3O4	-266.61	LA-001	34.97	LA-001	627.00		S-S	LA-001
					1594.00	32.97	S-L	
GA	.00		9.82	LA-001	29.78	1.33	S-L	LA-001
GAS	-46.40	LA-001,KU-001	16.22	TR-003	965.00		S-L	LA-001,NB-003
GA2O3	-261.05	MA-003,TR-010	20.22	LA-001,NB-002	1725.00		S-L	LA-001
GA2S3	-136.80	KU-001	27.21	TR-003				
GA2(CO3)3			46.40	TR-003				
GA2(SO3)3			55.40	TR-003				
GA2(SO4)3			63.50	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
GE	.00		7.43	LA-001	937.20	7.12	S-L	LA-001
GEO(GAS)	-22.79	LA-001	52.51	LA-001				
GEO2	-129.15	LA-001	13.20	LA-001	707.00	42.05	S-S	LA-001
					1115.00	10.49	S-L	
GES	-21.40	KU-001,TR-010	15.77	CA-084,KU-001	625.00	5.97	S-L	LA-001,CA-072,
					760.00		L-G	KU-001
GES2			19.00	CA-072	825.00	10.00	S-L	CA-072
GE(CO3)2			34.20	KE-001				
GE(SO3)2			43.20	KE-001				
GE(SO4)2			35.30	TR-003				
HF	.00		10.91	LA-001	1550.00		S-S	LA-001
					2222.00	5.21	S-L	
HFO2	-273.60	HU-006,TR-010	14.17	LA-001	2790.00		S-L	LA-001
HFS2			19.80	TR-003				
HF(CO3)2			34.90	KE-001				
HF(SO3)2			43.90	KE-001				
HF(SO4)2			38.80	TR-003				
H2	.00	JA-001	31.21	JA-001				
H2O(GAS)	-57.77	LA-001	45.07	LA-001				
IR	.00		8.50	LA-001	2443.00		S-L	LA-001
IRO2	-53.00	KU-001,TR-010	17.20	LA-001				
IRS2	-34.00	HE-002,TR-010	15.00	HE-002				
IRS3	-26.30	KU-001,LA-001	20.30	LA-001				
IR(SO4)2			39.20	TR-003				
IR2S3	-58.00	HE-002,TR-010	23.00	HE-002,TR-010				
K	.00		15.37	LA-001	63.20	.56	S-L	LA-001
					753.80	18.51	L-G	
KALO2	-271.46	TR-002	18.50	TR-003				
KFEO2	-165.50	TR-002	22.03	TR-003				
KVO3	-277.33	TR-002	29.90	KE-001				
K2CO3	-271.87	LA-001	36.07	LA-001	250.00		S-S	LA-001
					428.00		S-S	
					622.00		S-S	
					901.00	7.79	S-L	

					TRANSITION DATA			
COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
K2CRO4	-319.72	TR-002	47.60	KE-001				
K2CR2O4	-541.19	TR-002	44.10	KE-001				
K2MOO4	-356.90	TR-002	43.55	TR-007				
K2O	-86.36	LA-001	23.48	LA-001				
K2S	-87.86	LA-001,TR-010	26.34	TR-003	146.40	.09	S-S	LA-001,KU-001
					834.00		S-L	
K2SO3	-266.90	NB-003	37.40	TR-003				
K2SO4	-342.34	LA-001	41.97	LA-001	595.00	2.25	S-S	LA-001,CA-002
					1069.00	8.75	S-L	
K2TIO3	-384.60	CA-063	32.90	TR-003				
K2WO4	-390.84	TR-002	42.50	TR-007				
LA	.00		13.69	LA-001	548.00		S-S	LA-001
					709.00		S-S	
					920.00	2.70	S-L	
LAS	-108.00	ST-002	18.80	TR-003				
LAS2	-145.00	KU-001,TR-010	18.82	TR-003				
LA2O3	-430.50	HU-001,TR-010	30.56	LA-001	2315.00		S-L	LA-001
					4200.00		L-G	
LA2S3	-282.00	KU-001,TR-010	32.41	TR-003				
LA2(CO3)3			51.60	TR-003				
LA2(SO3)3			60.60	TR-003				
LA2(SO4)3	-939.80	WI-001	68.70	TR-003				
LI	.00		6.70	LA-001	180.50	.72	S-L	LA-001
LIALO2	-284.29	KU-001,LA-001	12.69	LA-001,KU-001				
LIFEO2	-173.70	KU-001	18.00	KU-001				
LIVO3	-281.48	TR-002	23.10	KE-001				
LI2CO3	-290.26	LA-001	21.58	LA-001	410.00		S-S	LA-001
					720.00		S-L	
LI2CRO4	-333.53	TR-002	34.00	KE-001				
LI2CR2O4	-501.89	TR-002	30.60	KE-001				
LI2MOO4	-375.52	TR-002	32.15	TR-007				
LI2O	-142.50	LA-001	9.05	LA-001	1727.00	17.99	S-L	LA-001
					2327.00		L-G	
LI2S	-107.40	KU-001	14.94	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
LI2SO3	-279.40	CA-001	26.00	TR-003				
LI2SO4	-342.58	LA-001	35.36	LA-001	575.00	6.78	S-S	LA-001
					857.00	1.85	S-L	
LI2TIO3	-394.03	TR-002	21.90	LA-001,KU-001				
LI2WO4	-396.56	TR-002	31.10	TR-007				
MG	.00		7.78	LA-001	649.50	2.14	S-L	LA-001
					1120.00	31.49	L-G	
MGAL2O4	-551.00	CA-048,CA-049	19.25	KU-001	2135.00		S-L	KU-001
MGCO3	-263.98	JA-001,LA-001	15.70	JA-001,LA-001				
MGCRO4	-307.08	TR-002	32.00	TR-003				
MGCR2O4	-453.10	CA-038,TR-010	25.30	KU-001,LA-001	2200.00		S-L	KU-001
MGFE2O4	-349.20	CA-042,CA-047	28.28	LA-001	392.00		S-S	LA-001
					957.00	.35	S-S	
MGMOO4	-334.80	CA-077,TR-010	28.40	CA-017				
MGO	-143.63	LA-001,NB-003	6.40	LA-001,NB-003	2802.00	18.49	S-L	LA-001
MGS	-83.00	CA-019,NB-003	10.60	LA-001				
MGSO3	-241.00	NB-003	22.50	TR-003				
MGSO4	-305.50	JA-001	21.90	JA-001	1127.00	3.50	S-L	JA-001
MGTIO3	-371.50	CA-043	17.80	KU-001,LA-001				
MGTI2O5	-600.10	CA-043	30.40	KU-001,LA-001				
MGV2O6	-527.90	CA-050	38.27	CA-051				
MGWO4	-373.40	CA-044	26.86	TR-003				
MG2TIO4			24.80	KU-001				
MN	.00		7.59	LA-001	727.00	.54	S-S	LA-001
					1101.00	.54	S-S	
					1137.00	.43	S-S	
					1244.00	3.49	S-L	
MNAL2O4	-501.10	CA-027	25.18	TR-003	1577.00		S-L	CA-027
MNCO3	-213.74	LA-001	20.47	LA-001				
MNCRO4	-256.88	TR-002	34.75	TR-003				
MNCR2O4	-396.72	TR-002	29.82	TR-003				
MNFE2O4	-293.00	CA-028	31.97	TR-003				
MNMOO4	-284.40	CA-029	31.27	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TYPE	REFERENCES
MNO	-91.93	LA-001	14.26	LA-001	-155.40		S-S	LA-001
					1780.00	13.00	S-L	
MNO2	-124.16	LA-001	12.69	LA-001	250.00		S-S	LA-001
MNS	-49.45	LA-001	18.68	LA-001	1530.00	6.31	S-L	LA-001
MNSO3	-197.37	TR-002	24.40	ER-002				
MNSO4	-253.95	LA-001	26.78	LA-001	460.00	.57	S-S	LA-001,CA-002
					700.00		S-L	
MNS2	-49.50	KU-001	15.32	TR-003				
MNTIO3	-324.30	TR-002	23.20	TR-003				
MNV2O6	-484.18	TR-002	42.38	TR-003				
MNWO4	-312.60	CA-030	29.56	TR-003				
MN(SO4)2			34.30	TR-003				
MN2O3	-229.11	LA-001	26.40	LA-001	600.00		S-S	LA-001
MN2(AL2O4)3	-1430.00	TR-002	68.40	KE-001				
MN2(CO3)3	-545.46	TR-002	44.60	TR-003				
MN2(CRO4)3	-688.01	TR-002	96.60	KE-001				
MN2(CR2O4)3	-1080.20	TR-002	86.40	KE-001				
MN2(FE2O4)3	-810.67	TR-002	96.60	KE-001				
MN2(MOO4)3	-818.86	TR-002	69.20	TR-007				
MN2(SO3)3	-502.39	TR-002	53.60	TR-003				
MN2(SO4)3	-666.90	WI-001	61.70	TR-003				
MN2(TIO3)3	-906.26	TR-002	60.60	KE-001				
MN2(V2O6)3	-1369.60	TR-002	133.20	KE-001				
MN2(WO4)3	-862.24	TR-002	66.80	TR-007				
MN3O4	-331.12	LA-001	35.72	LA-001	1172.00	4.49	S-S	LA-001
					1590.00		S-L	
MO	.00		6.83	LA-001	2622.00	6.59	S-L	LA-001
MOO2	-140.83	LA-001	11.06	LA-001				
MOO3	-177.88	LA-001	18.57	LA-001	795.00	12.54	S-L	LA-001
					1155.00	32.97	L-G	
MOS2	-60.40	KU-001,TR-010	16.00	KU-001,LA-001				
MOS3	-61.47	LA-001	15.89	LA-001				
MO(CO3)3			50.10	KE-001				
MO(SO3)3			63.60	TR-003				

```
   COMPOUND        HEAT  OF    REFERENCES       ABSOLUTE     REFERENCES
                   FORMATION                    ENTROPY                                 TRANSITION DATA
                   25 DEG.C                     CAL/GMOLE/                    TEMP.     HEAT    TYPE   REFERENCES
                   KCAL/GMOLE                   DEG. K                        DEG.C     KCAL/
                                                                                        GMOLE

MO(SO4)3                                          67.80    KE-001
MO2S3               -92.50   KU-001,TR-010        28.00    KU-001,LA-001
NA                     .00                        12.28    LA-001              97.82      .62   S-L   LA-001
                                                                              890.00    21.27   L-G
NAALO2             -270.67   LA-001,KU-001        16.89    LA-001,KU-001
NAFEO2             -166.40   TR-002               21.10    LA-001,KU-001
NAVO3              -276.47   CA-041               27.40    KE-001
NA2CO3             -269.72   LA-001,JA-001        32.49    LA-001,JA-001      356.00            S-S   LA-001,JA-001
                                                                              486.00            S-S
                                                                              618.00            S-S
                                                                              854.00     7.88   S-L
NA2CRO4            -318.60   CA-069               42.60    KE-001
NA2CR2O4           -508.14   TR-002               39.20    KE-001
NA2MOO4            -354.00   CA-045               38.10    CA-017
NA2MO2O7           -539.40   CA-045               59.90    CA-046
NA2O               -102.87   LA-001               16.99    LA-001             920.00    11.20   S-L   LA-001
NA2S                -92.40   KU-001,TR-010        22.48    LA-001             950.00     1.19   S-L
NA2SO3             -260.40   CA-003,LA-001        34.88    LA-001
NA2SO4             -330.64   LA-001               35.69    LA-001             259.00     2.64   S-S   LA-001,CA-002
                                                                              884.00     6.86   S-L
NA2TIO3            -379.50   CA-063               29.10    KU-001,LA-001      287.00      .40   S-S   KU-001,LA-001
                                                                             1030.00    16.80   S-L
NA2TI2O5                                          41.47    KU-001,LA-001      985.00    26.20   S-L   KU-001,LA-001
NA2TI3O7                                          55.90    KU-001,LA-001     1128.00    37.10   S-L   KU-001
NA2WO4             -382.60   CA-045               39.10    TR-007
NA2W2O7            -597.30   CA-045               60.80    CA-046
NB                     .00                         8.72    LA-001            2487.00     6.40   S-L   LA-001
NBO                -116.11   LA-001               11.99    LA-001
NBO2               -189.93   LA-001               13.02    LA-001
NB2O5              -455.10   LA-001               32.78    LA-001             800.00            S-S   LA-001
                                                                             1100.00            S-S
                                                                             1512.00    24.58   S-L
NB2S5                                             51.80    KE-001
NB2(CO3)5                                         85.30    KE-001
```

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA			
					TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
NB2(SO3)5			107.80	KE-001				
NB2(SO4)5			114.80	KE-001				
NI	.00		7.13	LA-001	357.20	.14	S-S	LA-001
					1455.00	4.25	S-L	
NIAL2O4	-463.32	CA-037	25.38	TR-003				
NICO3	-162.98	LA-001	21.00	LA-001				
NICRO4	-216.48	TR-002	34.95	TR-003				
NICR2O4	-348.74	TR-002	30.02	TR-003				
NIFE2O4	-256.50	CA-036	30.08	LA-001	582.00		S-S	CA-056,LA-001
NIMOO4	-260.26	TR-002	30.77	TR-003				
NIO	-57.26	LA-001	9.08	LA-001	250.00		S-S	LA-001
					1960.00	12.09	S-L	
NIS	-20.20	KU-001,TR-010	12.66	CA-084,TR-010	396.00		S-S	KU-001
NISO3	-155.86	TR-002	25.40	TR-003				
NISO4	-213.50	LA-001	18.59	LA-001				
NITIO3	-287.75	CA-035,CA-055	19.48	CA-035				
NIV2O6	-443.59	TR-002	42.58	TR-003				
NIWO4	-271.62	CA-030	29.76	TR-003				
NI3S2	-47.50	KU-001,TR-010	32.00	CA-084,TR-010	550.00		S-S	KU-001
					1984.00		S-L	
NO	21.59	LA-001	50.31	LA-001				
NO2	7.96	LA-001	57.29	LA-001				
N2O4	2.24	LA-001	72.70	LA-001				
N2(GAS)	.00	JA-001	45.77	JA-001				
O2	.00		48.97	LA-001				
PB	.00		15.51	LA-001	327.40	1.14	S-L	LA-001
					1751.00	42.88	L-G	
PBAL2O4	-459.57	TR-002	30.38	TR-003				
PBCO3	-167.23	LA-001,NB-002	31.27	LA-001,NB-002				
PBCO3•PBO	-219.84	LA-001	48.47	LA-001				
PBCO3•2PBO	-272.82	LA-001	64.98	LA-001				
PBCRO4	-217.50	LA-001	39.95	TR-003	707.00		S-S	LA-001
PBCR2O4	-357.23	TR-002	35.02	TR-003				
PBFE2O4	-251.22	TR-002	37.17	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
PBMOO4	-265.65	LA-001	35.77	TR-003	1065.00		S-L	LA-001
PBO	-52.37	LA-001	15.60	LA-001	489.00		S-S	LA-001
					890.00	2.80	S-L	
					1472.00	50.89	L-G	
PBO•PBSO4	-275.20	KE-003	51.97	KE-003	970.00		S-L	LA-001
PBO2	-66.08	LA-001	18.26	LA-001				
PBS	-22.52	LA-001,NB-003	21.79	NB-003,LA-001	1114.00	4.16	S-L	LA-001,NB-003
PBSO3	-157.00	CA-006	30.40	TR-003				
PBSO4	-219.33	LA-081	35.17	LA-001	881.00	7.30	S-S	LA-001,CA-002
					1087.00	9.60	S-L	
PBTIO3	-285.34	TR-002	28.41	TR-003	490.00	1.15	S-S	LA-001,KU-001
					1170.00		S-L	
PBV2O6	-445.55	TR-002	47.58	TR-003				
PBWO4	-277.49	TR-002	34.76	TR-003				
PB(SO4)2			39.50	TR-003				
PB3O4	-175.47	LA-001	50.46	LA-001				
PD	.00		9.03	LA-001	1555.00	4.11	S-L	LA-001
PDCO3			24.09	TR-003				
PDO	-27.60	HE-002,TR-010	13.37	LA-001				
PDS	-18.00	HE-002	17.72	TR-003				
PDSO3			27.60	TR-003				
PDSO4			28.70	TR-003				
PDS2	-19.00	HE-002	17.72	TR-003				
RB2CO3	-269.48	LA-001	39.83	TR-003	303.00		S-S	LA-001
					873.00		S-L	
RB2O	-78.84	LA-001	26.50	TR-003	567.00	8.50	S-L	LA-001
RB2S	-83.20	NB-003,KU-001	31.70	TR-003				
RB2SO3	-265.32	TR-002	42.80	TR-003				
RB2SO4	.00	LA-001,NB-003	47.53	TR-003	650.00		S-S	LA-001,CA-002
					881.00	2.11	S-S	
					1074.00		S-L	
RE	.00		8.88	LA-001	3180.00	9.08	S-L	LA-001
REO2	-101.46	LA-001	17.39	LA-001				
REO3	-145.94	LA-001	19.30	LA-001	160.00		S-L	LA-001

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TYPE	REFERENCES
RES2	-42.70	CA-074,TR-010	19.22	LA-001				
RES3	-49.80	KU-001	23.00	KU-001				
RE2O7	-295.76	LA-001	49.52	LA-001	300.30	15.80	S-L	LA-001
					360.30	17.70	L-G	
RE2O8	-148.24	LA-001			150.00		S-L	LA-001
RE2S7	-107.90	CA-074,KU-001	48.00	KU-001				
RH	.00		7.55	LA-001	1960.00		S-L	LA-001
RHCO3			23.89	TR-003				
RHO	-23.89	LA-001	12.90	LA-001				
RHS			17.52	TR-003				
RHSO3			27.40	TR-003				
RHSO4			28.50	TR-003				
RH2O	-22.67	LA-001	27.70	TR-003				
RH2O3	-70.95	LA-001	26.50	TR-003				
RH2S			32.94	TR-003				
RH2SO4			48.69	TR-003				
RH2S3			29.80	TR-003				
RH2(SO4)3			66.10	TR-003				
RU	.00		6.82	LA-001	1035.00	.03	S-S	LA-001
					1200.00		S-S	
					1500.00	.23	S-S	
					2500.00		S-L	
RUO2	-72.20	CA-082,CA-083	12.50	CA-016				
RUO3(GAS)	-18.00	CA-016	63.70	CA-016				
RUO4(GAS)	-46.70	CA-016	65.50	CA-016,OR-001				
RUS2	-40.00	KU-001,TR-010	10.40	HE-002,TR-010				
S	.00	NB-003,JA-001	7.63	LA-001,NB-003	95.31	.10	S-S	LA-001
					101.00	.00	S-S	
					115.18	.41	S-L	
					444.60		L-G	
SB	.00		10.92	LA-001	94.60		S-S	LA-001
					413.00		S-S	
					630.90	4.88	S-L	
SB2O3	-169.40	CA-060	31.65	CA-010				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA			
					TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
SB204	-216.90	CA-060,TR-010	30.20	LA-001				
SB205	-210.23	LA-001	29.89	LA-001				
SB2S3	-40.50	KU-001,TR-010	43.50	CA-073,TR-010	546.00	5.60	S-L	LA-001,KU-001
SB2(AL204)3	-1362.50	TR-002	71.40	KE-001				
SB2(CO3)3	-468.09	TR-002	50.40	TR-003				
SB2(CRO4)3	-611.09	TR-002	99.60	KE-001				
SB2(CR2O4)3	-997.12	TR-002	89.40	KE-001				
SB2(FE2O4)3	-737.07	TR-002	99.60	KE-001				
SB2(MOO4)3	-740.01	TR-002	75.00	TR-007				
SB2(SO3)3	-420.64	TR-002	59.40	TR-003				
SB2(SO4)3	-574.20	NB-001,WI-001	67.50	TR-003				
SB2(TIO3)3	-839.04	TR-002	63.60	KE-001				
SB2(V2O6)3	-1294.40	TR-002	136.20	KE-001				
SB2(WO4)3	-785.00	TR-002	72.60	TR-007				
SC	.00	KR-001	8.20	KE-004,LA-001				
SC2O3	-456.16	HU-004,TR-010	18.40	CA-014				
SC2(CO3)3			43.40	TR-003				
SC2(SO3)3			52.40	TR-003				
SC2(SO4)3			60.50	TR-003				
SI	.00		4.47	LA-001	1423.00	11.11	S-L	LA-001
SIO(GAS)	-23.20	KU-001,LA-001	50.55	KU-001				
SIO2	-217.72	KU-001,TR-010	10.00	LA-001,NB-002	867.00	.12	S-S	LA-001
					1610.00	2.04	S-L	
SIS(GAS)	16.93	JA-001	53.43	JA-001				
SIS2	-49.00	JA-001,KU-001	18.00	KE-001,TR-003	1090.00		S-L	
SI(CO3)2			31.20	KE-001				
SI(SO3)2			40.20	KE-001				
SI(SO4)2			32.10	TR-003				
SN	.00		12.28	LA-001	18.00	.60	S-S	LA-001
					202.80	.00	S-S	
					231.90	1.69	S-L	
SNCO3			24.49	TR-003				
SNO	-68.33	LA-001,NB-002	13.56	LA-001,NB-002	1465.00	38.46	L-G	LA-001
SNO2	-138.75	LA-001,NB-001	12.50	LA-001,NB-001	410.00	.45	S-S	LA-001

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
SNS	-24.32	LA-001,WI-001	18.40	LA-001,KU-001	584.00	.16	S-S	LA-001,KU-001
					880.00	7.55	S-L	
SNSO3			28.00	TR-003				
SNSO4			29.10	TR-003				
SNS2	-39.90	LA-001,KU-001	20.88	LA-001,KU-001				
SN(AL2O4)2	-926.28	TR-002	40.90	KE-001				
SN(CO3)2	-330.04	TR-002	33.90	KE-001				
SN(CRO4)2	-425.63	TR-002	59.70	KE-001				
SN(CR2O4)2	-684.03	TR-002	52.90	KE-001				
SN(FE2O4)2	-507.28	TR-002	59.70	KE-001				
SN(MOO4)2	-509.39	TR-002	39.00	TR-007				
SN(SO3)2	-295.36	TR-002	42.90	KE-001				
SN(SO4)2	-393.40	NB-004,WI-001	37.10	TR-003				
SN(TIO3)2	-577.14	TR-002	35.70	KE-001				
SN(V2O6)2	-884.00	TR-002	84.10	KE-001				
SN(WO4)2	-542.46	TR-002	37.70	TR-007				
SO2	-70.93	LA-001	59.27	LA-001				
SO3	-94.41	LA-001	61.16	LA-001				
SR	.00		13.00	LA-001	589.00	.20	S-S	LA-001
					770.00	2.20	S-L	
					1367.00	33.18	L-G	
SRAL2O4	-559.81	CA-022	26.88	TR-003				
SRCO3	-290.98	LA-001	23.17	LA-001	924.00	.40	S-S	LA-001
					1497.00		S-L	
SRCRO4	-333.36	TR-002	36.45	TR-003				
SRCR2O4	-514.63	TR-002	31.52	TR-003				
SRFE2O4	-356.06	TR-002	33.67	TR-003				
SRMOO3	-308.60	CA-024						
SRMOO4	-375.20	TR-002	32.27	TR-003				
SRO	-140.74	LA-001,CA-007	13.00	LA-001	2460.00	16.70	S-L	LA-001
					3200.00	126.62	L-G	
SRS	-108.10	KU-001,TR-010	16.50	KU-001,LA-001				
SRSO3	-279.40	CA-006	26.90	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
SRSO4	-344.97	LA-001	29.07	LA-001	1152.00		S-S	LA-001,CA-002
					1605.00		S-L	
SRTIO3	-393.50	TR-002	25.99	LA-001				
SRV2O6	-562.96	TR-002	44.08	TR-003				
SRWO4	-393.00	CA-023	28.30	CA-023				
SR2TIO4			38.00	KU-001,LA-001				
S(GAS)	52.80	LA-001	40.09	LA-001				
TA	.00		9.89	LA-001	2996.00	7.50	S-L	LA-001
TA2O5	-488.50	KU-001,TR-010	34.15	LA-001	1320.00		S-S	LA-001
					1880.00		S-L	
TA2S5			53.20	KE-001				
TA2(CO3)5			86.70	KE-001				
TA2(SO3)5			109.20	KE-001				
TA2(SO4)5			116.20	KE-001				
TH	.00		12.75	LA-001	225.00		S-S	LA-001
					1400.00	.67	S-S	
					1695.00	3.74	S-L	
THO2	-294.09	LA-001	15.59	LA-001	2950.00		S-L	LA-001
					4400.00		L-G	
THS	-99.96	LA-001	20.92	TR-003				
THS2	-109.89	LA-001	20.92	TR-003	1905.00		S-L	LA-001,KU-001
TH(AL2O4)2	-1101.50	TR-002	44.50	KE-001				
TH(CO3)2	-519.62	TR-002	37.50	KE-001				
TH(CRO4)2	-614.33	TR-002	63.30	KE-001				
TH(CR2O4)2	-884.49	TR-002	56.50	KE-001				
TH(FE2O4)2	-687.28	TR-002	63.30	KE-001				
TH(MOO4)2	-701.89	TR-002	41.80	TR-007				
TH(SO3)2	-493.41	TR-002	46.50	KE-001				
TH(SO4)2	-607.26	CA-011	35.40	CA-011				
TH(TIO3)2	-752.68	TR-002	39.30	KE-001				
TH(V2O6)2	-1068.60	TR-002	87.70	KE-001				
TH(WO4)2	-731.63	TR-002	40.50	TR-007				
TH2S3	-258.60	LA-001,NB-003	36.60	TR-003	1950.00		S-L	LA-001,KU-001

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
TI	.00		7.32	LA-001	882.00	.95	S-S	JA-001,LA-001
					1668.00	3.70	S-L	
TICO3			21.19	TR-003				
TIO	-123.85	LA-001	8.30	LA-001	991.00	.82	S-S	LA-001
					2020.00	13.98	S-L	
TIO2	-225.50	LA-001	12.00	LA-001	1855.00	15.48	S-L	LA-001
TISO3			24.70	TR-003				
TISO4			25.80	TR-003				
TIS2	-80.00	KU-001	18.73	LA-001,KU-001	147.00		S-S	KU-001
TI(SO4)2			33.80	TR-003				
TI2O3	-362.65	LA-001,JA-001	18.82	LA-001,JA-001	200.00	.22	S-S	LA-001,JA-001
					2130.00	38.46	S-L	
TI2(CO3)3			43.60	TR-003				
TI2(SO3)3			52.60	TR-003				
TI2(SO4)3			60.70	TR-003				
TI3O5	-586.74	LA-001	30.89	LA-001	177.00	.22	S-S	LA-001
U	.00		12.02	LA-001	662.00	.70	S-S	LA-001
					772.00	1.14	S-S	
					1133.00	4.71	S-L	
					2730.00		S-L	LA-001
UO2	-258.97	LA-001	18.62	LA-001				
UO2SO4	-451.20	OW-001	36.57	OW-001				
UO3	-291.70	LA-001	23.55	LA-001				
US	-91.00	CA-075,KU-001	18.00	KU-001	2462.00		S-L	CA-075
US2	-120.00	KU-001	26.00	KU-001	1350.00		S-S	KU-001
					1680.00		S-L	
U(AL2O4)2	-1063.00	TR-002	48.00	KE-001				
U(CO3)2	-478.20	TR-002	41.00	KE-001				
U(CRO4)2	-573.04	TR-002	66.80	KE-001				
U(CR2O4)2	-839.08	TR-002	60.00	KE-001				
U(FE2O4)2	-650.72	TR-002	66.80	KE-001				
U(MOO4)2	-660.57	TR-002	41.90	TR-007				
U(SO3)2	-451.00	TR-002	50.00	KE-001				
U(SO4)2	-563.00	WI-001	40.00	TR-003				
U(TIO3)2	-714.04	TR-002	42.80	KE-001				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
U(V2O6)2	-1027.20	TR-002	91.20	KE-001				
U(WO4)2	-689.78	TR-002	40.60	TR-007				
U2S3	-224.00	KU-001	35.00	KU-001				
U3O8	-854.10	KU-001	67.50	KU-001,LA-001				
V	.00		7.00	LA-001	1730.00	4.18	S-L	LA-001
VCO3			21.49	TR-003				
VO	-97.95	LA-001	9.29	LA-001	3100.00		L-G	LA-001
VOSO4	-313.10	FL-001	27.10	FL-001				
VS	-44.91	LA-001	14.50	LA-001	1900.00		S-L	LA-001
VSO3			25.00	TR-003				
VSO4			26.10	TR-003				
V2O3	-289.79	LA-001	23.48	LA-001	1967.00		S-L	LA-001
V2O4	-343.78	LA-001	24.30	LA-001	72.00	2.05	S-S	LA-001
					1542.00	27.19	S-L	
					2700.00		L-G	
V2O5	-372.68	LA-001,NB-003	31.27	LA-001,NB-003	670.00	15.55	S-L	LA-001
					1800.00		L-G	
V2S3			25.00	TR-003				
V2S4			30.20	TR-003				
V2S5			50.20	KE-001				
V2(CO3)3			44.10	TR-003				
V2(SO3)3			53.20	TR-003				
V2(SO4)3			61.30	TR-003				
W	.00		7.83	LA-001	3377.00	8.42	S-L	JA-001
WO2	-140.90	KU-001,TR-010	16.01	LA-001				
WO3	-201.46	JA-001	18.14	JA-001	777.00	.41	S-S	JA-001
					1472.00	17.55	S-L	
					1667.00	20.70	L-G	
WS2	-53.97	CA-070,TR-010	28.90	CA-070,TR-010				
W(CO3)2			33.10	KE-001				
W(CO3)3			49.70	KE-001				
W(SO3)2			42.10	KE-001				
W(SO3)3			63.20	KE-001				
W(SO4)2			39.00	TR-003				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES	TRANSITION DATA TEMP. DEG.C	TRANSITION DATA HEAT KCAL/ GMOLE	TRANSITION DATA TYPE	TRANSITION DATA REFERENCES
W(SO4)3			67.40	KE-001				
Y	.00	LA-001	10.99	LA-001				
Y2O3	-455.34	LA-001,KU-001	23.68	LA-001,KU-001				
Y2(CO3)3			48.00	TR-003				
Y2(SO3)3			57.00	TR-003				
Y2(SO4)3			65.10	TR-003				
ZN	.00		9.94	LA-001	419.50	1.74	S-L	LA-001
					907.00	27.40	L-G	
ZNAL2O4	-485.00	TR-002	25.78	TR-003				
ZNCO3	-193.68	LA-001,NB-003	19.69	LA-001,NB-003				
ZNCRO4	-239.65	TR-002	35.35	TR-003				
ZNCR2O4	-372.83	TR-002	30.42	TR-003				
ZNFE2O4	-279.60	CA-028,TR-010	32.20	KU-001,LA-001				
ZNMOO4	-283.39	TR-002	31.17	TR-003				
ZNO	-83.38	LA-001	10.39	LA-001	1975.00	12.49	S-L	LA-001
ZNO•2ZNSO4	-551.36	IN-002	66.44	IN-002				
ZNS	-48.50	LA-001,NB-003	13.80	LA-001,NB-003				
ZNSO3	-178.48	TR-002	25.80	TR-003				
ZNSO4	-233.69	LA-001,NB-003	29.77	LA-001,NB-003	754.00	4.74	S-S	CA-002
ZNTIO3	-309.30	CA-039	24.21	TR-003				
ZNV2O6	-466.75	TR-002	42.98	TR-003				
ZNWO4	-327.00	CA-040	33.80	CA-040				
ZN2TIO4	-391.90	CA-039	32.78	LA-001,KU-001				
ZR	.00	LA-001	9.29	LA-001	862.00	.91	S-S	LA-001
					1855.00	4.78	S-L	
ZRO2	-261.36	LA-001	12.02	LA-001				
ZRS2			17.12	TR-003				
ZR(AL2O4)2	-1078.30	TR-002	39.50	KE-001				
ZR(CO3)2	-502.61	TR-002	32.50	KE-001				
ZR(CRO4)2	-596.97	TR-002	58.30	KE-001				
ZR(CR2O4)2	-879.29	TR-002	51.50	KE-001				
ZR(FE2O4)2	-661.04	TR-002	58.30	KE-001				
ZR(MOO4)2	-684.18	TR-002	38.00	TR-007				
ZR(SO3)2	-478.52	TR-002	41.50	KE-001				

COMPOUND	HEAT OF FORMATION 25 DEG.C KCAL/GMOLE	REFERENCES	ABSOLUTE ENTROPY CAL/GMOLE/ DEG. K	REFERENCES		TRANSITION DATA		
					TEMP. DEG.C	HEAT KCAL/ GMOLE	TYPE	REFERENCES
ZR(SO4)2	-597.01	LA-001	36.10	TR-003				
ZR(TIO3)2	-729.98	TR-002	34.30	KE-001				
ZR(V2O6)2	-1051.90	TR-002	82.70	KE-001				
ZR(WO4)2	-716.02	TR-002	36.70	TR-007				

HEAT CAPACITY (CAL/GMOLE/DEG.K)

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	 BX10**3	 CX10**6	 DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
AG	5.38	1.74	.00	-.17	25.00	TO	961.28	LA-001,PE-001
	7.50	.00	.00	.00	961.28	TO	1200.00	
AGVO3	31.11	3.88	.00	7.45	25.00	TO	700.00	TR-004
AG2AL2O4	39.66	11.38	.00	7.92	25.00	TO	700.00	TR-004
AG2CO3	19.57	24.36	.00	.00	25.00	TO	227.00	LA-001,KE-002
AG2CRO4	34.54	12.44	.00	4.96	25.00	TO	700.00	TR-004
AG2CR2O4	41.78	9.24	.00	3.74	25.00	TO	700.00	TR-004
AG2FE2O4	39.71	21.79	.00	5.60	25.00	TO	700.00	TR-004
AG2MOO4	33.31	12.94	.00	3.68	25.00	TO	700.00	TR-004
AG2O	13.25	7.04	.00	.00	25.00	TO	700.00	LA-001
AG2S	10.13	26.40	.00	.00	25.00	TO	179.00	KU-001,LA-001
	21.64	.00	.00	.00	179.00	TO	577.00	
AG2SO3	20.16	22.14	.00	.00	25.00	TO	700.00	TR-001
AG2SO4	23.39	27.58	.00	.24	25.00	TO	657.00	LA-001
AG2TIO3	30.39	8.02	.00	3.50	25.00	TO	700.00	TR-004
AG2WO4	35.55	8.97	.00	4.80	25.00	TO	700.00	TR-004
AL	4.95	2.95	.00	.01	25.00	TO	658.60	LA-001,PE-001
	7.00	.00	.00	.00	658.60	TO	727.00	
AL2O3	26.40	4.34	.00	7.92	25.00	TO	700.00	LA-001,NB-002
AL2S						TO		
AL2S3	31.99	.98	.00	7.28	25.00	TO	700.00	TR-009
AL2TIO5	43.54	5.28	.00	11.42	25.00	TO	700.00	TR-004
AL2(CO3)3	65.57	21.94	.00	25.23	25.00	TO	700.00	TR-001
AL2(CRO4)3	90.26	20.54	.00	22.79	25.00	TO	700.00	TR-004
AL2(CR2O4)3	111.98	10.93	.00	19.14	25.00	TO	700.00	TR-004
AL2(FE2O4)3	105.78	48.60	.00	24.74	25.00	TO	700.00	TR-004
AL2(MOO4)3	86.59	22.03	.00	18.96	25.00	TO	700.00	TR-004
AL2(SO3)3	47.14	49.64	.00	7.92	25.00	TO	700.00	TR-001

```
DATE 27  FEB.  1969        HEAT CAPACITY (CAL/GMOLE/DEG.K) CONTINUED                       PAGE:     2

                           EQUATION  CP =  A  +  BT  +  CT**2  -  D/T**2

   COMPOUND                        COEFFICIENTS                            TEMPERATURE  RANGE       REFERENCES
                    A              BX10**3       CX10**6   DX10**-5       DEGREES CENTIGRADE

AL2(SO4)3          87.51          14.96          .00       26.66       25.00    TO     700.00  LA-001
AL2(TIO3)3         77.80           7.28          .00       18.41       25.00    TO     700.00  TR-004
AL2(V2O6)3        173.32           6.52          .00       52.64       25.00    TO     700.00  TR-004
AL2(WO4)3          93.30          10.13          .00       22.31       25.00    TO     700.00  TR-004
AS                  5.23           2.22          .00         .01       25.00    TO     500.00  LA-001,PE-001

AS2O3               8.37          48.60          .00         .00       25.00    TO     300.00  KU-001
AS2O5                                                                           TO
AS2S3              13.95          45.20          .00        -.64       25.00    TO     300.00  TR-009
AS2S5                                                                           TO
AS2(CO3)3          47.54          66.20          .00       17.31       25.00    TO     300.00  TR-001

AS2(SO3)3          29.10          93.90          .00         .00       25.00    TO     300.00  TR-001
AS2(SO4)3          36.27         101.80          .00        1.74       25.00    TO     300.00  TR-001
B                   1.46           4.52          .00        -.04       25.00    TO     700.00  LA-001,PE-001
BA                  5.43           3.15          .00         .07       25.00    TO     370.00  LA-001
                    2.46           6.98          .00        -.17      370.00    TO     710.00
                    7.50            .00          .00         .00      710.00    TO    1200.00
BAAL2O4            39.14           5.38          .00        9.91       25.00    TO     700.00  TR-004

BACO3              20.76          11.69          .00        4.77       25.00    TO     700.00  LA-001
BACRO4             34.02           6.44          .00        6.94       25.00    TO     700.00  TR-004
BACR2O4            41.26           3.24          .00        5.72       25.00    TO     700.00  TR-004
BAFE2O4            39.19          15.79          .00        7.59       25.00    TO     700.00  TR-004
BAMOO3                                                                          TO

BAMOO4             32.79           6.94          .00        5.66       25.00    TO     700.00  TR-004
BAO                12.73           1.04          .00        1.98       25.00    TO     700.00  LA-001
BAS                14.59           -.08          .00        1.77       25.00    TO     700.00  TR-009
BASO3              19.64          16.14          .00        1.98       25.00    TO     700.00  TR-001
BASO4              33.76            .03          .00        8.39       25.00    TO     700.00  LA-001

BATIO3             29.03           2.04          .00        4.58       25.00    TO    1500.00  KU-001
BAV2O6             61.70           1.76          .00       16.89       25.00    TO     700.00  TR-004
BAWO4              35.02           2.97          .00        6.80       25.00    TO     700.00  TR-004
```

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
BA2TIO4	42.60	3.06	.00	7.46	25.00	TO	700.00	TR-004
BE	4.61	2.09	.00	1.13	25.00	TO	1200.00	LA-001,PE-001
BEAL2O4	34.85	8.34	.00	11.09	25.00	TO	700.00	TR-004
BECO3	21.50	9.87	.00	8.94	25.00	TO	700.00	TR-001
BECRO4	29.73	9.40	.00	8.12	25.00	TO	700.00	TR-004
BECR2O4	36.97	6.20	.00	6.91	25.00	TO	700.00	TR-004
BEFE2O4	34.90	18.75	.00	8.77	25.00	TO	700.00	TR-004
BEMOO4	28.51	9.90	.00	6.85	25.00	TO	700.00	TR-004
BEO	8.45	4.00	.00	3.17	25.00	TO	700.00	LA-001,CA-012
BES	10.31	2.88	.00	2.95	25.00	TO	700.00	TR-009
BESO3	15.36	19.10	.00	3.17	25.00	TO	700.00	TR-001
BESO4	14.47	28.32	.00	2.15	25.00	TO	600.00	CA-005
BETIO3	25.58	4.98	.00	6.67	25.00	TO	700.00	TR-004
BEV2O6	57.42	4.72	.00	18.07	25.00	TO	700.00	TR-004
BEWO4	30.74	5.93	.00	7.96	25.00	TO	700.00	TR-004
BI	4.48	5.40	.00	-.00	25.00	TO	271.30	LA-001,PE-001
	7.50	.00	.00	.00	271.30	TO	700.00	
BI2O3	24.73	8.00	.00	.00	25.00	TO	500.00	LA-001
BI2S3	28.89	6.10	.00	.01	25.00	TO	600.00	KU-001,LA-001
BI2(AL2O4)3	103.94	21.02	.00	23.77	25.00	TO	500.00	TR-004
BI2(CO3)3	63.89	25.59	.00	17.31	25.00	TO	500.00	TR-001
BI2(CRO4)3	88.58	24.19	.00	14.87	25.00	TO	700.00	TR-004
BI2(CR2O4)3	110.30	14.59	.00	11.22	25.00	TO	500.00	TR-004
BI2(FE2O4)3	95.16	63.77	.00	10.64	25.00	TO	500.00	TR-004
BI2(MOO4)3	84.91	25.69	.00	11.04	25.00	TO	500.00	TR-004
BI2(SO3)3	45.46	53.30	.00	.00	25.00	TO	500.00	TR-001
BI2(SO4)3	52.63	61.22	.00	1.74	25.00	TO	500.00	TR-001
BI2(TIO3)3	76.12	10.93	.00	10.49	25.00	TO	500.00	TR-004
BI2(V2O6)3	164.27	19.69	.00	39.64	25.00	TO	500.00	TR-004

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
BI2(WO4)3	91.62	13.78	.00	14.39	25.00	TO	500.00	TR-004
BO(GAS)						TO		
BS(GAS)	5.96	4.73	-2.12	.00	25.00	TO	727.00	JA-001
B2O3	8.73	25.40	.00	1.31	25.00	TO	700.00	LA-001
B2S3	14.32	22.03	.00	.67	25.00	TO	310.00	TR-009
C	2.90	2.49	.00	1.48	25.00	TO	727.00	JA-001
	6.02	.04	.00	9.15	727.00	TO	1727.00	
CA	5.02	3.74	.00	-.12	25.00	TO	440.00	LA-001,PE-001
	1.29	7.97	.00	-1.97	440.00	TO	700.00	
CAAL2O4	36.00	5.96	.00	7.96	25.00	TO	1500.00	KU-001
CAAL4O7	66.09	5.48	.00	17.80	25.00	TO	1500.00	KU-001
CACO3	24.97	5.24	.00	6.20	25.00	TO	700.00	LA-001
CACRO4	33.14	6.48	.00	6.62	227.00	TO	627.00	TR-004
CACR2O4	40.37	3.27	.00	5.40	25.00	TO	600.00	TR-004
CAFE2O4	39.39	4.76	.00	3.66	25.00	TO	1200.00	LA-001,KU-001
CAMOO3						TO		
CAMOO4	31.92	6.98	.00	5.35	227.00	TO	627.00	TR-004
CAO	11.86	1.08	.00	1.66	227.00	TO	627.00	LA-001
CAS	10.20	3.80	.00	.00	25.00	TO	727.00	KU-001,LA-001,
						TO		TR-009
CASO3	18.77	16.18	.00	1.66	25.00	TO	600.00	TR-001
CASO4	17.22	23.37	.00	.33	25.00	TO	700.00	LA-001,NB-003
CATIO3	30.47	1.36	.00	6.69	25.00	TO	1260.00	KU-001
CAV2O6	58.36	4.98	.00	14.87	25.00	TO	600.00	TR-004
CAWO4	34.15	3.07	.00	6.47	227.00	TO	627.00	TR-004
CA(OH)2	25.13	2.88	.00	4.51	25.00	TO	700.00	LA-001
CA2FE2O5	47.18	20.75	.00	6.87	25.00	TO	600.00	TR-004
CD	4.77	3.73	.00	-.36	25.00	TO	321.00	LA-001,PE-001
	7.10	.00	.00	.00	321.00	TO	700.00	
CDAL2O4	36.05	6.42	.00	7.92	25.00	TO	700.00	TR-004
CDCO3	22.70	7.94	.00	5.77	25.00	TO	700.00	TR-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
CDCRO4	30.93	7.48	.00	4.96	25.00	TO	700.00	TR-004
CDCR2O4	38.17	4.28	.00	3.74	25.00	TO	700.00	TR-004
CDFE2O4	36.10	16.83	.00	5.60	25.00	TO	700.00	TR-004
CDMOO4	29.71	7.98	.00	3.68	25.00	TO	700.00	TR-004
CDO	9.65	2.09	.00	.00	25.00	TO	700.00	LA-001
CDS	12.93	.87	.00	.00	25.00	TO	700.00	LA-001,KU-001
CDSO3	16.56	17.18	.00	.00	25.00	TO	700.00	TR-001
CDSO4	18.49	18.48	.00	.01	25.00	TO	700.00	LA-001
CDTIO3	26.78	3.06	.00	3.50	25.00	TO	700.00	TR-004
CDV2O6	58.62	2.80	.00	14.91	25.00	TO	700.00	TR-004
CDWO4	31.94	4.01	.00	4.80	25.00	TO	700.00	TR-004
CE	5.93	3.74	.00	.10	25.00	TO	777.00	LA-001,PE-001
	8.00	.00	.00	.00	777.00	TO	2727.00	
CEO2	15.00	2.51	.00	.00	25.00	TO	1700.00	LA-001
CES						TO		
CES2	18.72	.27	.00	-.43	25.00	TO	1700.00	TR-009
CE(CO3)2	41.11	14.24	.00	11.54	25.00	TO	1700.00	TR-001
CE(SO3)2	28.83	32.71	.00	.00	25.00	TO	1700.00	TR-001
CE(SO4)2	33.61	37.99	.00	1.16	25.00	TO	1700.00	TR-001
CE2O3	25.17	6.33	.00	.00	300.00	TO	840.00	CA-018
CE2S3	30.75	2.97	.00	-.64	300.00	TO	840.00	TR-009
CE2(CO3)3	64.34	23.92	.00	17.31	300.00	TO	840.00	TR-001
CE2(SO3)3	45.90	51.63	.00	.00	300.00	TO	840.00	TR-001
CE2(SO4)3	53.07	59.55	.00	1.74	300.00	TO	840.00	TR-001
CE3S4						TO		
CO	5.79	2.47	.00	.59	25.00	TO	445.00	LA-001,PE-001
	-3.17	10.46	.00	-15.73	445.00	TO	700.00	
COAL2O4	37.93	6.38	.00	7.52	25.00	TO	700.00	TR-004
COCO3	24.59	7.91	.00	5.37	25.00	TO	1200.00	TR-001

```
                                  EQUATION  CP =  A  +  BT  +  CT**2  -  D/T**2

     COMPOUND                      COEFFICIENTS                              TEMPERATURE  RANGE         REFERENCES
                          A        BX10**3      CX10**6     DX10**-5         DEGREES CENTIGRADE

    COCRO4              32.82        7.44         .00         4.56       25.00    TO     700.00  TR-004
    COCR2O4             40.05        4.23         .00         3.33       25.00    TO    1200.00  TR-004
    COFE2O4             30.45       31.56         .00         3.01       25.00    TO     500.00  CA-056
                        48.27         .00         .00          .00      500.00    TO    1000.00
    COMOO4              31.59        7.94         .00         3.28       25.00    TO     700.00  TR-004
    COMPOUND                                                                      TO

    COO                 11.53        2.04         .00         -.40       25.00    TO    1200.00  LA-001
    COS                 10.69        2.41         .00          .03       25.00    TO     700.00  LA-001
    COSO3               18.44       17.14         .00         -.40       25.00    TO    1200.00  TR-001
    COSO4               30.09        9.91         .00          .01       25.00    TO     700.00  LA-001
    COTIO3              28.66        3.01         .00         3.09       25.00    TO    1200.00  TR-004

    COV2O6              65.39       -3.42         .00        17.94       25.00    TO    1200.00  TR-004
    COWO4               33.83        3.97         .00         4.40       25.00    TO    1200.00  TR-004
    CO2                  6.59        9.13       -2.65          .00       25.00    TO    1700.00  LA-001
    CO2S3                                                                         TO
    CO3O4               30.82       17.07         .00         5.76       25.00    TO     700.00  LA-001

    CO3S4               38.27       12.59         .00         4.90       25.00    TO     700.00  TR-009
    CR                   5.84        2.35         .00          .89       25.00    TO    1200.00  LA-001,PE-001
    CRO3                21.28        5.40         .00         4.96       25.00    TO     700.00  TR-008
    CR2O3               28.52        2.20         .00         3.74       25.00    TO    1200.00  LA-001
    CR2O7                                                                         TO

    CR2S3               34.12       -1.16         .00         3.10       25.00    TO    1200.00  TR-009
    CR2(CO3)3           67.69       19.80         .00        21.05       25.00    TO    1200.00  TR-001
    CR2(SO3)3           47.26       47.50         .00         3.74       25.00    TO    1200.00  TR-001
    CR2(SO4)3           56.43       55.42         .00         5.48       25.00    TO    1200.00  TR-001
    CS                   7.50         .00         .00          .00       25.00    TO      28.64  LA-001,PE-001
                         7.50         .00         .00          .00       28.64    TO     627.00

    CS2CO3                                                                        TO
    CS2O                                                                          TO
    CS2S                                                                          TO
```

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
CS2SO3						TO		
CS2SO4						TO		
CS2(G)	8.85	8.64	-3.29	.00	25.00	TO	1200.00	LA-001
CU	5.41	1.50	.00	-.00	25.00	TO	1084.00	LA-001,PE-001
	7.50	.00	.00	.00	1084.00	TO	1200.00	
CUAL2O4	35.67	9.14	.00	7.92	25.00	TO	700.00	TR-004
CUCO3	22.32	10.66	.00	5.77	25.00	TO	700.00	TR-001
CUCRO4	30.55	10.20	.00	4.96	25.00	TO	700.00	TR-004
CUCR2O4	37.79	7.00	.00	3.74	25.00	TO	700.00	TR-004
CUFEO2	20.67	10.23	.00	2.80	25.00	TO	700.00	TR-004
CUFE2O4	33.01	1.36	.00	1.44	25.00	TO	900.00	CA-079
CUMOO4	29.33	10.70	.00	3.68	25.00	TO	700.00	TR-004
CUO	9.27	4.80	.00	.00	25.00	TO	700.00	LA-001
CUO*CUSO4	28.07	21.97	.00	.03	25.00	TO	700.00	TR-004
CUS	11.13	3.68	.00	-.22	25.00	TO	700.00	TR-009,KE-002
CUSO3	16.18	19.90	.00	.00	25.00	TO	700.00	TR-001
CUSO4	18.81	17.18	.00	.03	25.00	TO	600.00	LA-001
CUTIO3	26.40	5.78	.00	3.50	25.00	TO	700.00	TR-004
CUVO3	31.93	3.21	.00	7.45	25.00	TO	700.00	TR-004
CUV2O6	58.24	5.52	.00	14.91	25.00	TO	700.00	TR-004
CUWO4	31.56	6.73	.00	4.80	25.00	TO	700.00	TR-004
CU2AL2O4	41.30	10.04	.00	7.92	25.00	TO	700.00	TR-004
CU2CO3	27.95	11.56	.00	5.77	25.00	TO	700.00	TR-001
CU2CRO4	36.18	11.10	.00	4.96	25.00	TO	700.00	TR-004
CU2CR2O4	43.42	7.90	.00	3.74	25.00	TO	700.00	TR-004
CU2MOO4	34.95	11.60	.00	3.68	25.00	TO	700.00	TR-004
CU2O	14.89	5.70	.00	.00	25.00	TO	700.00	LA-001
CU2S	19.49	.00	.00	.00	25.00	TO	103.00	LA-001
	23.24	.00	.00	.00	103.00	TO	350.00	
	20.31	.00	.00	.00	350.00	TO	700.00	

```
DATE 27  FEB.  1969        HEAT CAPACITY (CAL/GMOLE/DEG.K) CONTINUED                        PAGE:    8

                             EQUATION  CP =  A  +  BT  +  CT**2  -  D/T**2

   COMPOUND                     COEFFICIENTS                          TEMPERATURE  RANGE      REFERENCES
                     A          BX10**3     CX10**6    DX10**-5      DEGREES CENTIGRADE

 CU2SO3            21.80        20.80         .00        .00        25.00    TO      700.00  TR-001
 CU2SO4            24.19        23.40         .00        .58        25.00    TO      700.00  TR-001
 CU2TIO3           32.02         6.68         .00       3.50        25.00    TO      700.00  TR-004
 CU2WO4            37.19         7.63         .00       4.80        25.00    TO      700.00  TR-004
 C(O)               6.31         1.96        -.38        .00        25.00    TO     1700.00  LA-001

 FE                 4.13         6.38         .00        .00          .00    TO      760.00  PE-001
 FEAL2O4           38.05         6.34         .00       8.68        25.00    TO      700.00  TR-004
 FECO3             11.62        26.78         .00        .00        25.00    TO      500.00  LA-001
 FECRO4            32.94         7.40         .00       5.72        25.00    TO      700.00  TR-004
 FECR2O4           38.96         5.34         .00       7.62        25.00    TO     1500.00  LA-001,KU-001

 FEMOO4            31.72         7.90         .00       4.44        25.00    TO      700.00  TR-004
 FEO               11.66         2.00         .00        .76        25.00    TO     1200.00  LA-001
 FES                5.19        26.40         .00        .00        25.00    TO      138.00  KU-001,LA-001
                   17.40          .00         .00        .00       138.00    TO      325.00
                   12.20         2.38         .00        .00       325.00    TO     1195.00
 FESO3             18.57        17.10         .00        .76        25.00    TO     1200.00  TR-001
 FESO4             20.96        19.74         .00       1.34        25.00    TO     1200.00  TR-001

 FES2              18.00         1.18         .00       3.12        25.00    TO      700.00  LA-001,KU-001
 FETIO3            27.87         4.36         .00       4.79        25.00    TO     1370.00  LA-001,KU-001
 FEV2O6            65.51        -3.46         .00      19.09        25.00    TO     1200.00  TR-004
 FEWO4             33.95         3.93         .00       5.56        25.00    TO     1200.00  TR-004
 FE2O3             23.48        18.59         .00       3.55        25.00    TO      677.00  LA-001
                   35.98          .00         .00        .00       677.00    TO      767.00
                   31.70         1.76         .00        .00       767.00    TO     1200.00

 FE2TIO4           40.44         4.98         .00       5.02        25.00    TO     1200.00  TR-004
 FE2TIO5           40.61        19.57         .00       7.04        25.00    TO      677.00  TR-004
 FE2(AL2O4)3      105.67        27.77         .00      29.37        25.00    TO      700.00  TR-004
 FE2(CO3)3         82.93        11.33         .00      35.72        25.00    TO     1200.00  TR-001
 FE2(CRO4)3        90.31        30.95         .00      20.48        25.00    TO      700.00  TR-004

 FE2(CR2O4)3      129.34          .33         .00      29.63        25.00    TO     1200.00  TR-004
```

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
FE2(MOO4)3	86.64	32.45	.00	16.64	25.00	TO	700.00	TR-004
FE2(SO3)3	44.21	63.89	.00	3.55	25.00	TO	677.00	TR-001
FE2(SO4)3	51.38	71.81	.00	5.29	25.00	TO	600.00	TR-001
FE2(TIO3)3	95.16	-3.33	.00	28.90	25.00	TO	1200.00	TR-004
FE2(V2O6)3	205.32	-22.64	.00	73.42	25.00	TO	1200.00	TR-004
FE2(WO4)3	110.65	-.47	.00	32.80	25.00	TO	1200.00	TR-004
FE3O4	21.87	48.19	.00	.00	25.00	TO	627.00	LA-001
	47.97	.00	.00	.00	627.00	TO	1200.00	
GA	6.23	.00	.00	.00	25.00	TO	29.78	LA-001
	6.64	.00	.00	.00	29.78	TO	700.00	
GAS						TO		
GA2O3	11.77	25.18	.00	.00	25.00	TO	600.00	LA-001
GA2S3	17.34	21.82	.00	-.64	25.00	TO	600.00	TR-009
GA2(CO3)3	50.93	42.78	.00	17.31	25.00	TO	600.00	TR-001
GA2(SO3)3	32.50	70.48	.00	.00	25.00	TO	600.00	TR-001
GA2(SO4)3	39.67	78.40	.00	1.74	25.00	TO	600.00	TR-001
GE	5.94	.88	.00	.54	25.00	TO	937.20	LA-001
	7.00	.00	.00	.00	937.20	TO	1200.00	
GEO(GAS)						TO		
GEO2	11.19	7.17	.00	.00	25.00	TO	707.00	LA-001
GES	10.66	3.72	.00	.00	25.00	TO	1700.00	CA-072
GES2	14.14	6.25	.00	.00	25.00	TO	825.00	CA-072
GE(CO3)2	37.31	18.90	.00	11.54	25.00	TO	707.00	TR-001
GE(SO3)2	25.02	37.37	.00	.00	25.00	TO	700.00	TR-001
GE(SO4)2	29.80	42.65	.00	1.16	25.00	TO	700.00	TR-001
HF	5.73	1.19	.00	-.00	25.00	TO	1200.00	LA-001
HFO2	17.38	2.08	.00	3.48	25.00	TO	1200.00	LA-001
HFS2	21.11	-.16	.00	3.05	25.00	TO	1200.00	TR-009
HF(CO3)2	43.49	13.81	.00	15.02	25.00	TO	1200.00	TR-001
HF(SO3)2	31.20	32.28	.00	3.48	25.00	TO	1200.00	TR-001

HEAT CAPACITY (CAL/GMOLE/DEG.K) CONTINUED

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
HF(SO4)2	35.98	37.56	.00	4.64	25.00	TO	1200.00	TR-001
H2	6.94	-.19	.47	.00	25.00	TO	1200.00	JA-001
H2O(GAS)	6.78	3.57	-.46	.00	25.00	TO	2700.00	LA-001
IR	5.56	1.42	.00	.00	25.00	TO	1200.00	LA-001,PE-001
IRO2	9.17	15.19	.00	.00	25.00	TO	700.00	LA-001
IRS2	12.89	12.95	.00	-.43	25.00	TO	700.00	TR-009,WE-001
IRS3						TO		
IR(SO4)2	27.77	50.68	.00	1.16	25.00	TO	700.00	TR-001
IR2S3						TO		
K	7.16	.00	.00	.00	25.00	TO	63.20	LA-001
	8.91	-4.64	2.99	.00	63.20	TO	700.00	
KALO2	22.16	6.83	.00	4.16	25.00	TO	700.00	TR-004
KFEO2	29.84	2.67	.00	8.62	25.00	TO	900.00	TR-004
KVO3	36.23	1.57	.00	9.68	25.00	TO	900.00	TR-004
K2CO3	30.97	15.19	.00	6.17	25.00	TO	900.00	JA-001
K2CRO4	39.19	14.72	.00	5.36	25.00	TO	700.00	TR-004
K2CR2O4	46.44	11.52	.00	4.14	25.00	TO	900.00	TR-004
K2MOO4	37.97	15.22	.00	4.08	25.00	TO	700.00	TR-004
K2O	17.91	9.32	.00	.40	25.00	TO	900.00	LA-001
K2S	16.78	4.74	.00	.00	25.00	TO	547.00	DW-001
K2SO3	24.82	24.42	.00	.40	25.00	TO	1200.00	TR-001
K2SO4	28.76	23.79	.00	4.26	25.00	TO	595.00	LA-001
	33.59	13.40	.00	.00	595.00	TO	1069.00	
	47.78	.00	.00	.00	1069.00	TO	1200.00	
K2TIO3	35.04	10.30	.00	3.90	25.00	TO	900.00	TR-004
K2WO4	40.21	11.25	.00	5.20	25.00	TO	900.00	TR-004
LA	6.17	1.60	.00	.00	25.00	TO	548.00	LA-001,PE-001
LAS						TO		
LAS2						TO		
LA2O3	28.86	3.07	.00	3.27	25.00	TO	700.00	NB-003,LA-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS				TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
	A	BX10**3	CX10**6	DX10**-5				
LA2S3	34.44	-.29	.00	2.62	25.00	TO	700.00	TR-009
LA2(CO3)3	68.03	20.67	.00	20.58	25.00	TO	700.00	TR-001
LA2(SO3)3	49.59	48.37	.00	3.27	25.00	TO	700.00	TR-001
LA2(SO4)3	56.76	56.29	.00	5.01	25.00	TO	700.00	TR-001
LI	5.11	4.47	.00	.52	25.00	TO	180.50	LA-001
	8.46	-3.51	1.96	.00	180.50	TO	700.00	
LIALO2	20.66	5.21	.00	5.65	25.00	TO	700.00	TR-004
LIFEO2	20.70	10.42	.00	4.49	25.00	TO	700.00	TR-004
LIVO3	31.95	3.40	.00	9.14	25.00	TO	700.00	TR-004
LI2CO3	5.04	49.66	.00	-2.84	25.00	TO	410.00	JA-001
	4.31	42.42	.00	1.35	410.00	TO	720.00	
LI2CRO4	36.22	11.48	.00	8.33	25.00	TO	700.00	TR-004
LI2CR2O4	43.46	8.28	.00	7.12	25.00	TO	700.00	TR-004
LI2MOO4	34.99	11.98	.00	7.06	25.00	TO	700.00	TR-004
LI2O	14.93	6.08	.00	3.38	25.00	TO	700.00	LA-001
LI2S	16.79	4.96	.00	3.16	25.00	TO	700.00	TR-009
LI2SO3	21.84	21.18	.00	3.38	25.00	TO	700.00	TR-001
LI2SO4	24.23	23.82	.00	3.96	25.00	TO	700.00	TR-001
LI2TIO3	32.06	7.06	.00	6.88	25.00	TO	700.00	TR-004
LI2WO4	37.23	8.01	.00	8.17	25.00	TO	700.00	TR-004
MG	5.52	2.33	.00	.30	25.00	TO	649.50	LA-001,PE-001
	8.10	.00	.00	.00	649.50	TO	727.00	
MGAL2O4	36.80	6.40	.00	9.78	25.00	TO	1500.00	KU-001
MGCO3	18.61	13.79	.00	4.16	25.00	TO	427.00	JA-001,LA-001
MGCRO4	31.46	7.14	.00	6.44	25.00	TO	700.00	TR-004
MGCR2O4	40.20	3.56	.00	9.58	25.00	TO	1500.00	KU-001
MGFE2O4	21.05	44.55	.00	.00	25.00	TO	392.00	LA-001
	45.39	.00	.00	.00	392.00	TO	957.00	
	25.66	13.57	.00	.00	957.00	TO	1750.00	
MGMOO4	25.19	12.60	.00	.00	25.00	TO	827.00	CA-076

```
                              EQUATION  CP =  A  +  BT  +  CT**2  -  D/T**2

   COMPOUND                  COEFFICIENTS                               TEMPERATURE  RANGE       REFERENCES
                     A         BX10**3      CX10**6    DX10**-5        DEGREES CENTIGRADE

MGO                10.17         1.74         .00         1.48        25.00    TO     1727.00   LA-001
MGS                 9.24         2.50         .00         -.01        25.00    TO      700.00   JA-001
MGSO3              17.09        16.84         .00         1.48        25.00    TO      700.00   TR-001
MGSO4              16.53        21.80         .00          .02        25.00    TO     1127.00   JA-001
MGTIO3             28.29         3.28         .00         6.53        25.00    TO     1500.00   KU-001,LA-001

MGTI2O5            44.43         3.70         .00         8.48        25.00    TO     1200.00   TR-004
MGV2O6             64.03        -3.72         .00        19.81        25.00    TO     1200.00   TR-004
MGWO4              32.47         3.67         .00         6.27        25.00    TO     1200.00   TR-004
MG2TIO4            35.96         8.54         .00         6.89        25.00    TO     1545.00   KE-002
MN                  3.76         7.47         .00          .00          .00    TO      825.00   PE-001

MNAL2O4            37.50         6.28         .00         8.80        25.00    TO      700.00   TR-004
MNCO3              21.99         9.30         .00         4.69        25.00    TO      427.00   LA-001,KE-002
MNCRO4             32.39         7.34         .00         5.84        25.00    TO      700.00   TR-004
MNCR2O4            39.63         4.14         .00         4.62        25.00    TO     1200.00   TR-004
MNFE2O4            54.87        -4.32         .00        19.29        25.00    TO     1200.00   TR-004

MNMOO4             31.12         7.83         .00         4.56        25.00    TO      700.00   TR-004
MNO                11.10         1.94         .00          .88        25.00    TO     1200.00   LA-001
MNO2               16.59         2.44         .00         3.88        25.00    TO      500.00   LA-001
MNS                11.40         1.80         .00          .00        25.00    TO     1200.00   LA-001
MNSO3              18.01        17.04         .00          .88        25.00    TO     1200.00   TR-001

MNSO4              29.24         8.92         .00         7.04        25.00    TO      700.00   LA-001
MNS2               20.31          .20         .00         3.44        25.00    TO      500.00   TR-009
MNTIO3             28.24         2.92         .00         4.38        25.00    TO     1200.00   TR-004
MNV2O6             64.96        -3.52         .00        19.21        25.00    TO     1200.00   TR-004
MNWO4              33.39         3.87         .00         5.68        25.00    TO     1200.00   TR-004

MN(SO4)2           35.19        37.92         .00         5.04        25.00    TO      500.00   TR-001
MN2O3              24.73         8.38         .00         3.23        25.00    TO      700.00   LA-001
MN2(AL2O4)3       103.94        21.40         .00        27.00        25.00    TO      700.00   TR-004
MN2(CO3)3          63.89        25.97         .00        20.54        25.00    TO      700.00   TR-001
MN2(CRO4)3         88.58        24.57         .00        18.10        25.00    TO      700.00   TR-004
```

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
MN2(CR2O4)3	110.30	14.97	.00	14.44	25.00	TO	700.00	TR-004
MN2(FE2O4)3	104.10	52.64	.00	20.04	25.00	TO	700.00	TR-004
MN2(MOO4)3	84.91	26.07	.00	14.26	25.00	TO	700.00	TR-004
MN2(SO3)3	45.46	53.68	.00	3.23	25.00	TO	700.00	TR-001
MN2(SO4)3	52.63	61.60	.00	4.97	25.00	TO	700.00	TR-001
MN2(TIO3)3	76.12	11.31	.00	13.72	25.00	TO	700.00	TR-004
MN2(V2O6)3	171.64	10.55	.00	47.95	25.00	TO	700.00	TR-004
MN2(WO4)3	91.62	14.16	.00	17.62	25.00	TO	700.00	TR-004
MN3O4	34.62	10.82	.00	2.20	25.00	TO	1172.00	LA-001
	50.17	.00	.00	.00	1172.00	TO	1227.00	
MO	5.31	1.49	.00	-.00	25.00	TO	1200.00	LA-001,PE-001
MOO2						TO		
MOO3	20.06	5.90	.00	3.68	25.00	TO	700.00	LA-001
MOS2	11.20	13.50	.00	.00	25.00	TO	450.00	KE-002
MOS3	25.64	2.54	.00	3.03	25.00	TO	700.00	TR-009
MO(CO3)3	59.23	23.50	.00	20.99	25.00	TO	700.00	TR-001
MO(SO3)3	40.79	51.20	.00	3.68	25.00	TO	700.00	TR-001
MO(SO4)3	47.96	59.12	.00	5.42	25.00	TO	700.00	TR-001
MO2S3						TO		
NA	6.74	.00	.00	.00	25.00	TO	97.82	LA-001
	9.08	-5.02	2.87	.00	97.82	TO	700.00	
NAALO2	21.05	4.87	.00	3.96	25.00	TO	700.00	TR-004
NAFEO2	21.08	10.08	.00	2.80	25.00	TO	700.00	TR-004
NAVO3	32.33	3.06	.00	7.45	25.00	TO	700.00	TR-004
NA2CO3	2.63	58.33	.00	-5.85	25.00	TO	486.00	LA-001,JA-001
	12.08	30.68	.00	1.27	486.00	TO	854.00	
NA2CRO4	36.98	10.80	.00	4.96	25.00	TO	700.00	TR-004
NA2CR2O4	44.22	7.59	.00	3.74	25.00	TO	700.00	TR-004
NA2MOO4	35.75	11.28	.00	3.68	25.00	TO	700.00	TR-004
NA2MO2O7	55.79	17.17	.00	7.36	25.00	TO	700.00	TR-004

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
NA2O	15.69	5.40	.00	.00	25.00	TO	700.00	LA-001
NA2S	17.55	4.28	.00	-.22	25.00	TO	700.00	KE-002
NA2SO3	22.60	20.50	.00	.00	25.00	TO	700.00	LA-001,CA-004
NA2SO4	15.53	52.77	.00	.00	25.00	TO	259.00	LA-001
	29.05	19.33	.00	.00	259.00	TO	884.00	
	47.16	.00	.00	.00	884.00	TO	1200.00	
NA2TIO3	25.18	20.72	.00	.00	25.00	TO	287.00	KU-001,LA-001
	25.95	17.00	.00	.00	287.00	TO	1100.00	
NA2TI2O5	49.32	7.06	.00	4.60	25.00	TO	1000.00	KU-001
NA2TI3O7	63.46	10.64	.00	5.64	25.00	TO	1100.00	KU-001
NA2WO4	37.99	7.33	.00	4.80	25.00	TO	700.00	TR-004
NA2W2O7	60.28	9.25	.00	9.59	25.00	TO	700.00	TR-004
NB	5.66	.96	.00	-.00	25.00	TO	1200.00	LA-001
NBO						TO		
NBO2						TO		
NB2O5	36.22	5.54	.00	4.88	25.00	TO	1200.00	LA-001
NB2S5	45.53	-.07	.00	3.81	25.00	TO	1200.00	TR-009
NB2(CO3)5	101.49	34.87	.00	33.73	25.00	TO	1200.00	TR-001
NB2(SO3)5	70.77	81.04	.00	4.88	25.00	TO	1200.00	TR-001
NB2(SO4)5	82.72	94.24	.00	7.78	25.00	TO	1200.00	TR-001
NI	4.11	6.95	.00	.02	25.00	TO	357.20	LA-001,PE-001
	6.00	1.80	.00	-.01	357.20	TO	1200.00	
NIAL2O4	43.33	.23	.00	12.40	25.00	TO	700.00	TR-004
NICO3	25.87	6.57	.00	7.08	25.00	TO	1200.00	TR-001
NICRO4	38.21	1.29	.00	9.43	25.00	TO	700.00	TR-004
NICR2O4	41.34	2.90	.00	5.05	25.00	TO	1200.00	TR-004
NIFE2O4	31.62	28.25	.00	4.66	25.00	TO	582.00	CA-056
	48.68	.00	.00	.00	582.00	TO	1000.00	
NIMOO4	36.98	1.79	.00	8.16	25.00	TO	700.00	TR-004

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
NIO	-4.99	37.56	.00	-3.89	25.00	TO	250.00	LA-001
	11.18	2.02	.00	.00	250.00	TO	1200.00	
NIS	9.25	12.80	.00	.00	25.00	TO	327.00	LA-001,KU-001
NISO3	27.69	7.28	.00	-.58	25.00	TO	700.00	TR-001
NISO4	30.08	9.92	.00	.00	25.00	TO	700.00	LA-001
NITIO3	29.95	1.68	.00	4.81	25.00	TO	1200.00	TR-004
NIV2O6	66.67	-4.76	.00	19.65	25.00	TO	1200.00	TR-004
NIWO4	35.11	2.63	.00	6.11	25.00	TO	1200.00	TR-004
NI3S2						TO		
NO	6.42	2.13	-.47	.00	25.00	TO	1700.00	LA-001
NO2	10.26	2.04	*******	.00	25.00	TO	1700.00	LA-001
N2O4	11.74	28.30	-11.08	.00	25.00	TO	700.00	LA-001
N2(GAS)	6.30	1.83	-.33	.00	25.00	TO	1727.00	JA-001
O2	6.53	2.06	-.36	.00	25.00	TO	2700.00	LA-001
PB	5.67	2.26	.00	.02	25.00	TO	327.40	LA-001,PE-001
	7.86	.94	.21	.00	327.40	TO	700.00	
PBAL2O4	37.00	8.34	.00	7.92	25.00	TO	600.00	TR-004
PBCO3	23.65	9.87	.00	5.77	25.00	TO	600.00	TR-001
PBCO3*PBO						TO		
PBCO3*2PBO						TO		
PBCRO4	31.88	9.40	.00	4.96	25.00	TO	600.00	TR-004
PBCR2O4	39.12	6.20	.00	3.74	25.00	TO	600.00	TR-004
PBFE2O4	34.07	22.59	.00	3.55	25.00	TO	600.00	TR-004
PBMOO4	30.66	9.90	.00	3.68	25.00	TO	600.00	TR-004
PBO	10.60	4.00	.00	.00	25.00	TO	600.00	LA-001
PBO*PBSO4	21.55	35.01	.00	-4.21	25.00	TO	600.00	TR-004
PBO2	12.70	7.80	.00	.00	25.00	TO	700.00	LA-001
PBS	10.66	3.92	.00	.00	25.00	TO	600.00	KU-001,LA-001
PBSO3	17.51	19.10	.00	.00	25.00	TO	600.00	TR-001
PBSO4	10.94	31.01	.00	-4.20	25.00	TO	700.00	LA-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
PBTIO3	18.70	23.30	.00	.00	27.00	TO	600.00	KU-001
PBV2O6	57.11	7.90	.00	13.21	25.00	TO	600.00	TR-004
PBWO4	32.89	5.93	.00	4.80	25.00	TO	600.00	TR-004
PB(SO4)2	31.30	43.28	.00	1.16	25.00	TO	700.00	TR-001
PB3O4						TO		
PD	5.87	1.33	.00	.14	25.00	TO	1200.00	LA-001,PE-001
PDCO3	16.35	20.06	.00	5.77	25.00	TO	500.00	TR-001
PDO	3.30	14.19	.00	.00	25.00	TO	500.00	LA-001
PDS	5.16	13.07	.00	-.21	25.00	TO	500.00	TR-009
PDSO3	10.21	29.29	.00	.00	25.00	TO	700.00	TR-001
PDSO4	12.60	31.93	.00	.58	25.00	TO	500.00	TR-001
PDS2						TO		
RB2CO3	28.38	.00	.00	.00	25.00	TO	26.00	LA-001
RB2O						TO		
RB2S						TO		
RB2SO3						TO		
RB2SO4						TO		
RE	5.66	1.30	.00	-.00	25.00	TO	1200.00	LA-001,PE-001
REO2						TO		
REO3						TO		
RES2						TO		
RES3						TO		
RE2O7						TO		
RE2O8						TO		
RE2S7						TO		
RH	5.49	2.06	.00	.01	25.00	TO	1200.00	LA-001,PE-001
RHCO3	22.89	11.39	.00	5.77	25.00	TO	700.00	TR-001
RHO	9.84	5.53	.00	.00	25.00	TO	700.00	LA-001
RHS	11.70	4.41	.00	-.21	25.00	TO	700.00	TR-009

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
RHSO3	16.75	20.63	.00	.00	25.00	TO	700.00	TR-001
RHSO4	19.40	23.27	.00	.58	25.00	TO	700.00	TR-001
RH2O	15.60	6.47	.00	.00	25.00	TO	900.00	LA-001
RH2O3	20.72	13.78	.00	.00	25.00	TO	900.00	LA-001
RH2S	17.47	5.35	.00	-.21	25.00	TO	900.00	TR-009
RH2SO4	24.90	24.21	.00	.58	25.00	TO	600.00	TR-001
RH2S3	26.31	10.42	.00	-.64	25.00	TO	900.00	TR-009
RH2(SO4)3	48.62	67.01	.00	1.74	25.00	TO	600.00	TR-001
RU	5.24	1.50	.00	-.00	25.00	TO	727.00	LA-001
	7.20	.00	.00	.00	727.00	TO	1200.00	
RUO2						TO		
RUO3(GAS)						TO		
RUO4(GAS)						TO		
RUS2						TO		
S	5.41	.00	.00	.00	25.00	TO	115.18	JA-001
	7.46	-9.84	15.74	.00	115.18	TO	444.60	
	3.39	6.86	-.00	.00	444.60	TO	1200.00	
SB	5.50	1.76	.00	.00	25.00	TO	630.90	LA-001,PE-001
	7.50	.00	.00	.00	630.90	TO	700.00	
SB2O3	19.09	17.08	.00	.00	25.00	TO	900.00	LA-001
SB2O4	22.60	16.20	.00	.00	25.00	TO	700.00	LA-001
SB2O5						TO		
SB2S3	24.20	13.20	.00	.00	25.00	TO	648.00	KU-001,KE-002
SB2(AL2O4)3	98.30	30.10	.00	23.77	25.00	TO	700.00	TR-004
SB2(CO3)3	58.25	34.68	.00	17.31	25.00	TO	900.00	TR-001
SB2(CRO4)3	82.94	33.28	.00	14.87	25.00	TO	700.00	TR-004
SB2(CR2O4)3	104.66	23.67	.00	11.22	25.00	TO	900.00	TR-004
SB2(FE2O4)3	144.40	5.12	.00	50.51	25.00	TO	900.00	TR-004
SB2(MOO4)3	79.27	34.78	.00	11.04	25.00	TO	700.00	TR-004
SB2(SO3)3	39.82	62.38	.00	.00	25.00	TO	900.00	TR-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
SB2(SO4)3	46.99	70.30	.00	1.74	25.00	TO	900.00	TR-001
SB2(TIO3)3	70.48	20.02	.00	10.49	25.00	TO	900.00	TR-004
SB2(V2O6)3	182.75	-1.46	.00	56.86	25.00	TO	900.00	TR-004
SB2(WO4)3	85.98	22.87	.00	14.39	25.00	TO	900.00	TR-004
SC	6.12	1.45	.00	.43	25.00	TO	1500.00	KR-001
SC2O3	23.16	5.64	.00	.00	25.00	TO	1700.00	LA-001
SC2(CO3)3	62.32	23.24	.00	17.31	25.00	TO	1700.00	TR-001
SC2(SO3)3	43.89	50.94	.00	.00	25.00	TO	1700.00	TR-001
SC2(SO4)3	51.06	58.86	.00	1.74	25.00	TO	1700.00	TR-001
SI	5.80	.55	.00	1.09	25.00	TO	700.00	LA-001,PE-001
SIO(GAS)						TO		
SIO2	11.21	8.20	.00	2.70	25.00	TO	867.00	LA-001
	14.40	1.94	.00	.00	867.00	TO	1610.00	
SIS(GAS)	7.25	2.41	-.78	.00	25.00	TO	1700.00	JA-001
SIS2	22.80	-2.86	.00	8.60	25.00	TO	1610.00	TR-009,JA-001
SI(CO3)2	45.18	11.12	.00	20.57	25.00	TO	1610.00	TR-001
SI(SO3)2	25.03	38.40	.00	2.69	25.00	TO	867.00	TR-001
SI(SO4)2	29.81	43.68	.00	3.85	25.00	TO	867.00	TR-001
SN	4.43	6.28	.00	.00	25.00	TO	231.90	LA-001,PE-001
	7.30	.00	.00	.00	231.90	TO	700.00	
SNCO3	22.60	9.36	.00	5.77	25.00	TO	700.00	TR-001
SNO	9.55	3.50	.00	.00	25.00	TO	700.00	LA-001,NB-002
SNO2	17.65	2.40	.00	5.16	25.00	TO	1200.00	LA-001,NB-001
SNS	8.48	7.43	.00	-.95	25.00	TO	584.00	LA-001,KU-001
	9.78	3.74	.00	.00	584.00	TO	880.00	
SNSO3	16.46	18.60	.00	.00	25.00	TO	700.00	TR-001
SNSO4	18.85	21.24	.00	.58	25.00	TO	700.00	TR-001
SNS2	15.51	4.20	.00	.00	25.00	TO	700.00	LA-001,KU-001
SN(AL2O4)2	70.46	11.08	.00	21.00	25.00	TO	700.00	TR-004

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
SN(CO3)2	43.76	14.13	.00	16.70	25.00	TO	1200.00	TR-001
SN(CRO4)2	60.22	13.20	.00	15.07	25.00	TO	700.00	TR-004
SN(CR2O4)2	74.70	6.79	.00	12.63	25.00	TO	1200.00	TR-004
SN(FE2O4)2	105.18	-10.13	.00	41.98	25.00	TO	1200.00	TR-004
SN(MOO4)2	57.77	14.19	.00	12.52	25.00	TO	700.00	TR-004
SN(SO3)2	31.48	32.60	.00	5.16	25.00	TO	1200.00	TR-001
SN(SO4)2	36.26	37.88	.00	6.32	25.00	TO	1200.00	TR-001
SN(TIO3)2	51.91	4.36	.00	12.15	25.00	TO	1200.00	TR-004
SN(V2O6)2	125.36	-8.52	.00	41.83	25.00	TO	1200.00	TR-004
SN(WO4)2	62.25	6.26	.00	14.75	25.00	TO	1200.00	TR-004
SO2	7.02	9.75	-3.58	.00	25.00	TO	1200.00	LA-001
SO3	6.90	20.37	-7.12	.00	25.00	TO	1200.00	LA-001
SR	5.61	1.35	.00	.01	25.00	TO	700.00	LA-001
SRAL2O4	38.73	5.46	.00	9.73	25.00	TO	700.00	TR-004
SRCO3	21.41	8.56	.00	3.39	25.00	TO	700.00	LA-001
SRCRO4	33.62	6.52	.00	6.76	25.00	TO	700.00	TR-004
SRCR2O4	40.86	3.32	.00	5.54	25.00	TO	700.00	TR-004
SRFE2O4	38.79	15.87	.00	7.41	25.00	TO	700.00	TR-004
SRMOO3						TO		
SRMOO4	32.40	7.02	.00	5.48	25.00	TO	700.00	TR-004
SRO	12.33	1.12	.00	1.81	25.00	TO	700.00	LA-001
SRS	14.20	.00	.00	1.59	25.00	TO	700.00	TR-009
SRSO3	19.24	16.22	.00	1.81	25.00	TO	700.00	TR-001
SRSO4	21.79	13.30	.00	-.00	25.00	TO	1200.00	LA-001
SRTIO3	28.23	2.04	.00	4.58	25.00	TO	1500.00	LA-001,KU-001
SRV2O6	61.31	1.85	.00	16.71	25.00	TO	700.00	TR-004
SRWO4	34.62	3.05	.00	6.60	25.00	TO	700.00	TR-004
SR2TIO4	38.45	3.84	.00	4.67	25.00	TO	1500.00	KU-001,LA-001
S(GAS)	5.97	-1.26	.41	.00	25.00	TO	1700.00	LA-001
TA	6.28	.42	.00	.30	25.00	TO	1200.00	LA-001,PE-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
TA2O5	36.98	6.56	.00	5.95	25.00	TO	1200.00	LA-001
TA2S5	46.30	.95	.00	4.88	25.00	TO	1200.00	TR-009
TA2(CO3)5	102.26	35.89	.00	34.80	25.00	TO	1200.00	TR-001
TA2(SO3)5	71.53	82.06	.00	5.95	25.00	TO	1200.00	TR-001
TA2(SO4)5	83.48	95.26	.00	8.85	25.00	TO	1200.00	TR-001
TH	5.18	4.54	.00	.00	25.00	TO	1200.00	LA-001,PE-001
THO2	15.83	2.88	.00	1.60	25.00	TO	1200.00	LA-001
THS						TO		
THS2	19.55	.64	.00	1.16	25.00	TO	1200.00	TR-009
TH(AL2O4)2	68.64	11.56	.00	17.44	25.00	TO	700.00	TR-004
TH(CO3)2	41.94	14.61	.00	13.14	25.00	TO	1200.00	TR-001
TH(CRO4)2	58.40	13.68	.00	11.51	25.00	TO	700.00	TR-004
TH(CR2O4)2	72.88	7.27	.00	9.08	25.00	TO	1200.00	TR-004
TH(FE2O4)2	103.36	-9.65	.00	38.42	25.00	TO	1200.00	TR-004
TH(MOO4)2	55.95	14.68	.00	8.96	25.00	TO	700.00	TR-004
TH(SO3)2	29.65	33.08	.00	1.60	25.00	TO	1200.00	TR-001
TH(SO4)2	25.00	55.20	.00	.00	25.00	TO	637.00	CA-011
TH(TIO3)2	50.09	4.84	.00	8.59	25.00	TO	1200.00	TR-004
TH(V2O6)2	123.54	-8.04	.00	38.27	25.00	TO	1200.00	TR-004
TH(WO4)2	60.43	6.74	.00	11.19	25.00	TO	1200.00	TR-004
TH2S3						TO		
TI	6.38	1.13	.00	.69	25.00	TO	1668.00	JA-001
TICO3	22.90	10.24	.00	7.02	25.00	TO	1200.00	TR-001
TIO	10.56	3.60	.00	1.86	25.00	TO	991.00	LA-001
	11.84	3.01	.00	.00	991.00	TO	1200.00	
TIO2	17.13	.98	.00	3.50	25.00	TO	1200.00	LA-001
TISO3	17.47	18.70	.00	1.86	25.00	TO	1000.00	TR-001
TISO4	19.86	21.34	.00	2.44	25.00	TO	1000.00	TR-001
TIS2	8.08	27.34	.00	.00	25.00	TO	147.00	KU-001
	14.99	5.14	.00	.00	147.00	TO	737.00	

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
TI(SO4)2	35.73	36.46	.00	4.66	25.00	TO	1200.00	TR-001
TI2O3	7.31	53.49	.00	.00	25.00	TO	200.00	LA-001,JA-001
	34.66	1.30	.00	10.67	200.00	TO	1200.00	
TI2(CO3)3	74.18	18.61	.00	28.18	25.00	TO	1200.00	TR-001
TI2(SO3)3	55.97	40.05	.00	10.96	25.00	TO	1200.00	TR-001
TI2(SO4)3	63.14	53.97	.00	12.70	25.00	TO	1200.00	TR-001
TI3O5	35.45	29.48	.00	.00	25.00	TO	177.00	LA-001
	41.59	8.00	.00	.00	177.00	TO	700.00	
U	2.16	9.50	.00	-1.52	25.00	TO	662.00	LA-001,PE-001
	10.15	.00	.00	.00	662.00	TO	1133.00	
	9.15	.00	.00	.00	1133.00	TO	1200.00	
UO2	19.19	1.62	.00	3.96	25.00	TO	1200.00	LA-001
UO2SO4	26.90	26.00	.00	.00	25.00	TO	500.00	OW-001
UO3	22.08	2.54	.00	2.97	25.00	TO	600.00	LA-001
US						TO		
US2	15.20	8.70	.00	.00	25.00	TO	352.00	KU-001
U(AL2O4)2	72.00	10.30	.00	19.80	25.00	TO	700.00	TR-004
U(CO3)2	45.30	13.35	.00	15.50	25.00	TO	1200.00	TR-001
U(CRO4)2	61.76	12.42	.00	13.87	25.00	TO	700.00	TR-004
U(CR2O4)2	76.24	6.02	.00	11.43	25.00	TO	1200.00	TR-004
U(FE2O4)2	106.72	-10.91	.00	40.78	25.00	TO	1200.00	TR-004
U(MOO4)2	59.31	13.42	.00	11.31	25.00	TO	700.00	TR-004
U(SO3)2	33.01	31.82	.00	3.96	25.00	TO	1200.00	TR-001
U(SO4)2	37.79	37.10	.00	5.12	25.00	TO	1200.00	TR-001
U(TIO3)2	53.45	3.58	.00	10.95	25.00	TO	1200.00	TR-004
U(V2O6)2	126.90	-9.30	.00	40.63	25.00	TO	1200.00	TR-004
U(WO4)2	63.78	5.48	.00	13.55	25.00	TO	1200.00	TR-004
U2S3						TO		
U3O8	67.50	8.83	.00	11.94	25.00	TO	600.00	KU-001
V	4.96	2.42	.00	-.28	25.00	TO	1200.00	LA-001,PE-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	A	COEFFICIENTS BX10**3	CX10**6	DX10**-5	TEMPERATURE DEGREES		RANGE CENTIGRADE	REFERENCES
VCO3	24.37	9.08	.00	7.03	25.00	TO	1200.00	TR-001
VO	11.31	3.22	.00	1.26	25.00	TO	1200.00	LA-001
VOSO4	27.15	19.46	.00	4.52	72.00	TO	720.00	TR-001
VS	13.18	2.10	.00	1.04	25.00	TO	1200.00	TR-009
VSO3	18.22	18.32	.00	1.26	25.00	TO	1700.00	TR-001
VSO4	20.61	20.96	.00	1.84	25.00	TO	1200.00	TR-001
V2O3	29.34	4.76	.00	5.42	25.00	TO	1200.00	LA-001
V2O4	29.89	.00	.00	.00	25.00	TO	72.00	LA-001
	35.69	3.45	.00	7.89	72.00	TO	1200.00	
V2O5	46.51	3.90	.00	13.21	25.00	TO	670.00	LA-001,NB-003
	45.58	.00	.00	.00	670.00	TO	1200.00	
V2S3	34.93	1.40	.00	4.78	25.00	TO	1200.00	TR-009
V2S4	42.67	-.69	.00	6.15	25.00	TO	1200.00	TR-009
V2S5	63.17	-11.06	.00	17.26	25.00	TO	1200.00	TR-009
V2(CO3)3	68.50	22.36	.00	22.73	25.00	TO	1200.00	TR-001
V2(SO3)3	50.07	50.06	.00	5.42	25.00	TO	1700.00	TR-001
V2(SO4)3	57.24	57.98	.00	7.16	25.00	TO	1200.00	TR-001
W	5.85	.72	.00	.24	25.00	TO	3377.00	JA-001
WO2	15.49	3.58	.00	2.80	25.00	TO	2727.00	JA-001
WO3	20.81	3.81	.00	3.85	25.00	TO	777.00	JA-001
	20.80	2.76	.00	-.10	777.00	TO	1472.00	
	31.50	.00	.00	.00	1472.00	TO	1667.00	
WS2	21.55	-.36	.00	2.91	25.00	TO	1200.00	TR-009
W(CO3)2	41.60	15.31	.00	14.34	25.00	TO	2727.00	TR-001
W(CO3)3	57.45	23.13	.00	18.20	25.00	TO	1667.00	TR-001
W(SO3)2	31.65	32.09	.00	3.34	25.00	TO	700.00	TR-001
W(SO3)3	43.03	47.23	.00	4.80	25.00	TO	1200.00	TR-001
W(SO4)2	36.43	37.37	.00	4.50	25.00	TO	1200.00	TR-001
W(SO4)3	50.20	55.15	.00	6.54	25.00	TO	1200.00	TR-001
Y	5.59	1.90	.00	-.29	25.00	TO	1500.00	KU-001

EQUATION CP = A + BT + CT**2 - D/T**2

COMPOUND	COEFFICIENTS A	BX10**3	CX10**6	DX10**-5	TEMPERATURE RANGE DEGREES CENTIGRADE			REFERENCES
Y2O3	29.60	1.20	.00	4.78	25.00	TO	1000.00	KU-001
Y2(CO3)3	68.77	18.80	.00	22.09	25.00	TO	1000.00	TR-001
Y2(SO3)3	50.33	46.50	.00	4.78	25.00	TO	1000.00	TR-001
Y2(SO4)3	57.50	54.42	.00	6.52	25.00	TO	1000.00	TR-001
ZN	5.33	2.42	.00	-.01	25.00	TO	419.50	LA-001,PE-001
	7.48	.00	.00	.00	419.50	TO	700.00	
ZNAL2O4	38.11	5.56	.00	10.10	25.00	TO	700.00	TR-004
ZNCO3	24.76	7.08	.00	7.95	25.00	TO	1200.00	TR-001
ZNCRO4	32.99	6.62	.00	7.14	25.00	TO	700.00	TR-004
ZNCR2O4	25.49	21.69	.00	.00	25.00	TO	700.00	LA-001
ZNFE2O4	30.79	13.89	.00	.00	25.00	TO	700.00	LA-001
ZNMOO4	31.76	7.12	.00	5.86	25.00	TO	700.00	TR-004
ZNO	11.70	1.22	.00	2.18	25.00	TO	1200.00	LA-001
ZNO*2ZNSO4	45.82	42.79	.00	2.18	25.00	TO	700.00	TR-004
ZNS	12.16	1.24	.00	1.36	25.00	TO	927.00	LA-001,KU-001
ZNSO3	18.61	27.28	.00	2.18	25.00	TO	1200.00	TR-001
ZNSO4	17.06	20.79	.00	.00	25.00	TO	727.00	LA-001,NB-003
ZNTIO3	28.83	2.19	.00	5.66	25.00	TO	1200.00	TR-004
ZNV2O6	65.56	-4.24	.00	20.51	25.00	TO	1200.00	TR-004
ZNWO4	33.99	3.15	.00	6.97	25.00	TO	1200.00	TR-004
ZN2TIO4	39.80	5.54	.00	7.69	25.00	TO	1500.00	LA-001,KU-001
ZR	6.83	1.12	.00	.91	25.00	TO	862.00	KU-001
	7.27	.00	.00	.00	862.00	TO	1100.00	
ZRO2	16.63	1.80	.00	3.36	25.00	TO	700.00	LA-001
ZRS2	20.35	-.44	.00	2.92	25.00	TO	700.00	TR-009
ZR(AL2O4)2	69.44	10.48	.00	19.21	25.00	TO	700.00	TR-004
ZR(CO3)2	42.74	13.53	.00	14.90	25.00	TO	700.00	TR-001
ZR(CRO4)2	59.20	12.60	.00	13.27	25.00	TO	700.00	TR-004
ZR(CR2O4)2	73.68	6.19	.00	10.84	25.00	TO	700.00	TR-004
ZR(FE2O4)2	69.55	31.31	.00	14.57	25.00	TO	700.00	TR-004

```
                          EQUATION  CP =  A  +  BT  +  CT**2  -  D/T**2

  COMPOUND                     COEFFICIENTS                           TEMPERATURE  RANGE       REFERENCES
                     A         BX10**3      CX10**6    DX10**-5      DEGREES CENTIGRADE

ZR(MOO4)2          56.75        13.60         .00        10.72      25.00    TO      700.00   TR-004
ZR(SO3)2           30.45        32.00         .00         3.36      25.00    TO      700.00   TR-001

ZR(SO4)2           35.23        37.28         .00         4.52      25.00    TO      700.00   TR-001
ZR(TIO3)2          50.89         3.76         .00        10.35      25.00    TO      700.00   TR-004
ZR(V2O6)2         114.58         3.25         .00        33.17      25.00    TO      700.00   TR-004
ZR(WO4)2           61.23         5.66         .00        12.95      25.00    TO      700.00   TR-004
```

BIBLIOGRAPHY

AD-001 L. H. ADAMI, E. G. KING, U. S. BUR. MINES, REPT. OF INVEST. NO. 6617, (1965).

BA-001 R. F. BARROW, ET. AL., TRANS. FAR. SOC., VOL. 51, P. 1480, (1955).

BE-002 BERTHELOT, ESSAI DE MECANIQUE CHIMIQUE, PART 1, P. 319.

BI-001 W. BILTZ, Z. ELEKTROCHEM., VOL. 37, P. 498 (1931).

BI-002 W. BILTZ, Z. ANORG. CHEM., VOL. 71, P. 427 (1911).

BI-003 W. BILTZ, ET. AL., Z. ANORG. CHEM., VOL. 233, P. 257 (1937).

BO-001 J. BOUSQUET, G. PERACHON, COMPT. REND., VOL. 258, NO. 15, P. 3869 (1964).

BO-002 BOERICKE AND BANGERT, U. S. BUREAU OF MINES, REPT. OF INVEST. NO. 3813 (1945).

BR-001 L. BREWER, CHEMICAL REVIEWS, VOL. 52, P. 1 (1953).

BR-002 BRITZKE AND KAPUSTINSKII, Z. ANORG. CHEM., VOL. 194, P. 323, (1930).

BR-003 BRITZKE AND KAPUSTINSKII, J. PHYS. CHEM. (USSR), VOL. 5, P. 85, (1934).

BR-004 L. BREWER, L. BROMLEY, THE CHEMISTRY AND METALLURGY OF MISCELLANEOUS MATERIALS, (1950).

CA-001 CHEMICAL ABSTRACTS,64:8996A. A.A. SHIDLOVSKII, A.A. VOSKRESENSKII. ZH. FIZ. KHIM. VOL. 39, PP. 3097-9(1965).

BIBLIOGRAPHY (CONTINUED)

CA-002 CHEMICAL ABSTRACTS,64:7434D. T.R. INGRAHAM, P. MARIER. CAN. MET. QUART VOL. 4, PP. 169-76(1965).

CA-003 CHEMICAL ABSTRACTS,52:70E. N.A. LANDIYA, T. GRUZIN. POLITEKH. INST. PP. 43-9(1953).

CA-004 CHEMICAL ABSTRACTS,58:7432D A.A. FOTIEV. ZH. PRIKL. KHIM. VOL. 35, PP. 2402-9(1962).

CA-005 CHEMICAL ABSTRACTS,64:11950F. I.J.BEAR, A.G. TURNBULL, J. PHYS. CHEM. VOL. 70, PP. 711-17(1966).

CA-006 CHEMICAL ABSTRACTS,59:13403G. A.A. SHIDLOVSKII, A.A. VOSKRESENSKII. ZH. FIZ. KHIM, VOL. 37, PP. 2062-7(1963).

CA-007 CHEMICAL ABSTRACTS,65:19366F. G. V. FIDLIDER, ET AL. ZH. FIZ. KHIM. VOL. 40, PP. 2168-70(1966).

CA-008 CHEMICAL ABSTRACTS,54:6287A. H.W. GOLDSTEIN, ET AL. J. PHYS.CHEM. VOL. 63, PP. 1445-9(1959).

CA-009 CHEMICAL ABSTRACTS 64:1418G. R. BARANY, L.H. ADAMI, U. S. BUR. MINES, REPT. INVEST. NO. 6687(1965).

CA-010 CHEMICAL ABSTRACTS,65:3094B, E.A. GORGORAKI, V.V. TARASOV. TR. MOSK. KHIM.-TEKHNOL. INST. NO. 49, PP. 11-15(1965).

CA-011 CHEMICAL ABSTRACTS 54:19142C. S.W. MAYER, ET AL. J. PHYS. CHEM. VOL. 64, PP. 911-14 (1960). SEE TR-005 AND TR-006.

CA-012 CHEMICAL ABSTRACTS,64:4343A. M.A. GREENBAUM, ET AL. J. PHYS. CHEM. VOL. 69, PP. 4035-7(1965).

CA-013 CHEMICAL ABSTRACTS 65:17802F. H.BREKKEN. J. APPL. PHYS. VOL. 37, PP. 3635-6 (1966).

CA-014 CHEMICAL ABSTRACTS, 59:5860A W.W. WELLER, E.G. KING. U.S. BUR. MINES, REPT. INVEST. NO. 6245 (1963).

BIBLIOGRAPHY (CONTINUED)

CA-015 CHEMICAL ABSTRACTS 55:8023B. YA. I. GERASIMOV, ET AL. DOKL. AKAD. NAUK SSSR VOL. 134, PP. 1350-2(1960).

CA-016 CHEMICAL ABSTRACTS 59:14875H. W.E. BELL, M. TAGAMI, J. PHYS. CHEM. VOL. 67, PP. 2432-6 (1963).

CA-017 CHEMICAL ABSTRACTS 58:6257F. W.W. WELLER, E.G. KING U. S. BUR. MINES, REPT. INVEST. NO. 6147 (1963) .

CA-018 CHEMICAL ABSTRACTS,58:2908C. F.A. KUZNETSOV, T.N. REZUKHINA. ZH. FIZ. KHIM. VOL. 35, PP. 956-7 (1961).

CA-019 CHEMICAL ABSTRACTS,54:21971G. W.W. WELLER, E.G. KING, U. S. BUR. MINES REPT. INVEST. NO. 5590 (1960).

CA-020 CHEMICAL ABSTRACTS 65:9827D. N.G. BARANCHEEVA , L.A. ZHARKOVA. ZH. FIZ KHIM.VOL. 40, PP. 1368-70 (1966).

CA-021 CHEMICAL ABSTRACTS 64:16722G V.A. LEVITSKII, ET AL. ELEKTROKHIMIYA. VOL. 1, PP. 1371-4 (1965).

CA-022 CHEMICAL ABSTRACTS 54:17029G. C. BRISI, F. ABBATTISTA. ANN. CHIM. (ROME) VOL. 50, PP.165-9(1960). SEE TR-005

CA-023 CHEMICAL ABSTRACTS 59:7028H. V. A. LEVITSKII, T. N. REZUKHIMA. ZH. FIZ KHIM.VOL. 37, PP. 1135-7 (1963). SEE TR-005.

CA-024 CHEMICAL ABSTRACTS 61:1321E. L.A.ZHARKOVA, N.G. BARANCHEEVA. ZH. FIZ. KHIM. VOL. 38, PP. 752-4 (1964).

CA-025 CHEMICAL ABSTRACTS 65:95D. V.A. LEVITSKII, ET AL. IZV. AKAD.NAUK SSSR NEORGAN. MATERIALY. VOL. 2, PP. 325-31 (1966). SEE TR-005.

CA-026 CHEMICAL ABSTRACTS 56:13628A. F. MASSAZZA, ANN. CHIM. (ROME) VOL. 52, PP. 51-8.

CA-027 CHEMICAL ABSTRACTS 65:9822G. L.M. LENEV, I.A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, METALLY, PP. 73-8, (1966). SEE TR-005

BIBLIOGRAPHY (CONTINUED)

CA-028	CHEMICAL ABSTRACTS 65: 9831C. M. FISCHER. Z. ANORG. ALLGEM. CHEM. VOL. 345, PP. 134-6 (1966).
CA-029	CHEMICAL ABSTRACTS 63:1265F. R. BARANY. U. S. BUR. MINES, REPT. INVEST NO. 6618, (1965). SEE TR-005.
CA-030	CHEMICAL ABSTRACTS 56:2046C. Z.V. PROSHINA, T.N. REZUKHINA. ZHUR. NEORGAN. KHIM. VOL. 5, PP. 1016-21 (1960). SEE TR-005
CA-031	CHEMICAL ABSTRACTS 61:12705E. L. M. LENEV, I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, MET. I GORN. DELO, PP. 87-90 (1964) SEE TR-005.
CA-032	CHEMICAL ABSTRACTS 59:76F. T. N. REZUKHINA, V. A. LEVITSKII. ZH. FIZ. KHIM. VOL. 37, PP. 687-8 (1963) SEE TR-005.
CA-033	CHEMICAL ABSTRACTS 63:5007D A.N. GOLUBENKO, ET AL. ZH. FIZ. KHIM. VOL. 39, PP. 1164-7 (1965).
CA-034	CHEMICAL ABSTRACTS 63:7701D. V. A. LEVITSKII, ET AL. ELEKTROKHIMIYA VOL. 1, PP. 237-9 (1965). SEE TR-005.
CA-035	CHEMICAL ABSTRACTS 63:7701G. A. N. GOLUBENKO, T. N. REZUKHINA. ZH. FIZ. KHIM. VOL. 39, PP. 1519-21 (1965) SEE TR-005.
CA-036	CHEMICAL ABSTRACTS 63:6389D. Y. A. ZAIONCHKOVSKII, E. V. RUBAL'SKAYA. IZV. AKAD. NAUK SSSR, NEORGAN. MATERIALY. VOL. 1, PP. 257-9 (1965).
CA-037	CHEMICAL ABSTRACTS 64:1415A. L. M. LENEV, I. A. NOVOKHATSKII. ZH. NEORGAN. KHIM. VOL. 10, PP. 2400-3 (1965) SEE TR-005.
CA-038	CHEMICAL ABSTRACTS 59:2473D. I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR OTD. TEKHN. NAUK, MET. I GORN. DELO 1963.
CA-039	CHEMICAL ABSTRACTS 62:9867H. B. I. PANFILOV, N. N. FEODOS'EV. ZH NEORGAN. KHIM. VOL. 10 PP. 298-9 (1965). SEE TR-005.
CA-040	CHEMICAL ABSTRACTS 60:2389E. L. A. ZHARKOVA, ET AL. DOKL. AKAD. NAUK SSSR. VOL. 128, PP. 992-4 (1959).

BIBLIOGRAPHY (CONTINUED)

CA-041	CHEMICAL ABSTRACTS 55:7022H. H. KOEHLER, U.S. BUR. MINES, REPT. INVEST NO. 5700, (1960). SEE TR-005.
CA-042	CHEMICAL ABSTRACTS 55:11057C. L. A. REZNITSKII, K.G.KHOMYAKOV. DOKL. AKAD. NAUK SSSR., VOL. 131, PP. 325-6 (1960). SEE TR-005.
CA-043	CHEMICAL ABSTRACTS 56:15000H. A. S. BEREZHNOI, DOPOVIDI AKAD. NAUK UKR. RSR, PP. 65-8 (1962). SEE TR-005.
CA-044	CHEMICAL ABSTRACTS 60:2387E. T. N. REZUKHINA, V. A. LEVITSKII. ZH. FIZ KHIM. VOL. 37, PP. 2357-60 (1963) SEE TR-005.
CA-045	CHEMICAL ABSTRACTS 57:2927E. R. BARANY, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 5973 (1962). SEE TR-005.
CA-046	CHEMICAL ABSTRACTS 58:13212B. W. W. WELLER,K.K. KELLEY U. S. BUR. MINE REPT. INVEST. NO. 6191 (1963).
CA-047	CHEMICAL ABSTRACTS 57:13233C. L.A. REZNITSKII, K. G. KHOMYAKOV. VESTN. MOSK. UNIV., SER. II, KHIM. VOL. 15, PP. 28-30(1960) SEE TR-005.
CA-048	CHEMICAL ABSTRACTS 62:4696D. R. L. ALTMAN, J. PHYS. CHEM. VOL. 68 PP. 3425-6 (1964). SEE TR-005.
CA-049	CHEMICAL ABSTRACTS 64:7435D. O. J. KLEPPA,A. NAVROTSKY. INORGAN. CHEM. VOL 5, PP. 192-3 (1966) SEE TR-005.
CA-050	CHEMICAL ABSTRACTS 57:15893G.E. G. KING, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 6049 (1962) SEE TR-005.
CA-051	CHEMICAL ABSTRACTS 58:5103C. W. W. WELLER, E. G. KING, U.S. BUR. MINE REPT. INVEST. NO. 6130 (1962). SEE TR-006.
CA-052	CHEMICAL ABSTRACTS 56:10999H. W.W. WELLER, E. G. KING. U. S. BUR. MINES, REPT. INVEST. NO. 5954 (1961) .
CA-053	CHEMICAL ABSTRACTS 62:12509H. A.N. GOLUBENKO, T. N. REZUKHINA. ZH. FIZ KHIM. VOL. 38, PP. 2920-3 (1964).

BIBLIOGRAPHY (CONTINUED)

CA-054 CHEMICAL ABSTRACTS 61:5270C. L. M. LENEV, I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, MET. I GORN. DELO PP. 47-51 (1963). SEE TR-005

CA-055 CHEMICAL ABSTRACTS 64:7432G. I. A. NOVOKHATSKII, L. M. LENEV. IZV. VYSSHIKH. UCHEBN. ZAVEDENII, TSVETN. MET. VOL. 8 PP. 68-74. SEE TR-005

CA-056 CHEMICAL ABSTRACTS 66:89118C.N. A. LANDIYA, ET AL. IZV. AKAD. NAUK SSSR, NEORG. MATER. VOL. 2 , PP. 2050-7 (1966).

CA-057 CHEMICAL ABSTRACTS 66:69464J. D. BHOGESWARA RAO, V.V. DADAPE. J. PHYS. CHEM. VOL. 71, PP. 537-40(1967). SE TR-005.

CA-058 CHEMICAL ABSTRACTS 49:7419G. KUAN PAN J. CHINESE CHEM. SOC. (TAIWAN) SER II. VOL. 1, PP. 1-15 (1954).

CA-059 CHEMICAL ABSTRACTS 48:1131F. E.J. HUBER, C.E. HOLLEY J. AMER. CHEM. SOC. VOL. 75, PP. 3594-5 (1953).

CA-060 CHEMICAL ABSTRACTS 57:2927F. A. D. MAH U. S. BUR. MINES, REPT. INVEST. NO. 5972 (1962).

CA-061 CHEMICAL ABSTRACTS 56:13628A. F. MASSAZZA. ANN. CHIM. (ROME) VOL. 52, PP. 51-8 (1962).

CA-062 CHEMICAL ABSTRACTS 61:11662F. W. W. WELLER, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 6513 (1964).

CA-063 CHEMICAL ABSTRACTS 63:14148H. B. I. PANFILOV, N. N. FEODOS'EV, ZH. NEORGAN. KHIM. VOL. 10, PP. 1844-7 (1965).

CA-064 CHEMICAL ABSTRACTS 65:6386H. W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 6782 (1966).

CA-065 CHEMICAL ABSTRACTS 66:89119D. O. J. KLEPPA, ACTA. CHEM. SCAND. VOL. 20, PP. 2568-72 (1966).

CA-066 CHEMICAL ABSTRACTS 56:1008H. E. F. WESTRUM, A. F. BEALE, J. PHYS. CHEM. VOL. 65, PP. 353-5 (1961).

CA-067 CHEMICAL ABSTRACTS 58:60H. E. H. P. CORDFUNKE, G. MEYER, REC. TRAV. CHIM., VOL. 81, PP. 670-8 (1962).

CA-068 CHEMICAL ABSTRACTS 63:9122G. T. N. REZUKHINA, ET.AL., ELEKTROKHIMIYA VOL.1, PP.467-71 (1965). SEE TR-005.

CA-069 CHEMICAL ABSTRACTS 54:17028F. L.G. HELPER, ET AL, J. PHYS. CHEM., VOL. 64, PP.376-7(1960).

CA-070 CHEMICAL ABSTRACTS,54:10465F. E.ERDOS, ET AL. COLL. CZECH. CHEM. COMMUN., VOL.24, PP. 3836-43(1959).

CA-071 CHEMICAL ABSTRACTS,54:14904E. K.M.KOLBINA, ET AL. VESTNIK LENINGRAD UNIV., VOL.15, SER. KHIM. I FIZ., PP. 122-9(1960).

CA-072 CHEMICAL ABSTRACTS,61:7771G. G.A. BERGMAN, E.I.SCHMUK, IZV. AKAD. NAUK SSSR MET. I GORN. DELO, NO.3, PP.91-9(1964).

CA-073 CHEMICAL ABSTRACTS,57:13234C. W.W.WELLER, E.G.KING, U.S. BUR. MINES, REPT. INVEST. NO 6040 (1962).

CA-074 CHEMICAL ABSTRACTS,57:2927G. J.W.COBBLE,J.E.MCDONALD, J. PHYS. CHEM., VOL.66, P.791(1962).

CA-075 CHEMICAL ABSTRACTS,57:394C. E.D.CATER, ET AL. J. CHEM. PHYS., VOL. 35, PP. 608-18 (1961).

CA-076 CHEMICAL ABSTRACTS,58:8459B. T.N. REZUKHINA, ET AL, ZH. FIZ. KHIM., VOL. 35, PP.2639-42 (1961).

CA-077 CHEMICAL ABSTRACTS,58:5102C. R. BARANY, U. S. BUR. MINES, REPT. INVEST. NO 6143 (1962).

CA-078 CHEMICAL ABSTRACTS,55:8026G. L. REZNITSKII, K.G.KHOMYAKOV, VESTNIK MOSKOV. UNIV., SER. II, VOL.15, PP. 40-2 (1960).

CA-079 CHEMICAL ABSTRACTS,66:89104V. M. G. ZURAVLEVA, MATER. NAUCH. KONF. SOVNAR. NIZHNEV. EKON. RAIONA, VOLG. POLI. INST., VOL.2,PP236-9(1965).

BIBLIOGRAPHY (CONTINUED)

CA-080 CHEMICAL ABSTRACTS,68:69912. A.A.SHIDLOVSKII, A.A.VOSKRESENSKII, ZH. FIZ. KHIM., VOL.41, PP.1246-7 (1967).

CA-081 CHEMICAL ABSTRACTS,59:1256B. H. SCHAEFER, ET AL., Z. ANORG. ALLG. CHEM., VOL. 321, PP. 41-55 (1963).

CA-082 CHEMICAL ABSTRACTS,58:7586F. H. SCHAEFER,ET AL. Z. ANORG. ALLGEM. CHEM., VOL 319, PP. 327-36(1963).

CA-083 CHEMICAL ABSTRACTS,55:7023A. S.A. SHCHUKAREV, A.N. RYABOV, ZHUR. NEORG. KHIM., VOL. 5, PP.1931-3 (1960).

CA-084 CHEMICAL ABSTRACTS,61:12709B. K.K. KELLEY, W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 6511 (1964).

CA-085 CHEMICAL ABSTRACTS,56:12374E. T. N. REZUKHINA, ET AL., DOKL. AKAD.NAUK SSSR, VOL. 139, PP. 1405-8 (1961).

CH-001 J. CHIPMAN, J. AM. CHEM. SOC., VOL. 83, P. 1762 (1961).

CH-002 J. CHIPMAN, H. M. CHAN, TRANS. AMER. SOC. METALS, VOL. 38, P. 70 (1947).

CO-001 J.P. COUGHLIN, CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY, U. S. BUR. MINES BULL. 542 (1954).

CO-002 COURTOIS AND GASTEN, COMPT. REND., VOL. 207, P. 1220 (1938).

DW-001 A.S.DWORKIN, M.A.BREDIG, J. PHYS. CHEM., VOL.72, PP.1277-81(1968).

ER-001 E. ERDOS. THERMODYNAM. PROP. OF SULFITES,FIRST COMMUN. IN 'COLLECTION CZECHOSLOV. CHEM. COMMUN.,PRAGUE,VOL.27,PP.1428,1437(1962).

ER-002 E. ERDOS. THERMODYNAM. PROP. OF SULFITES,SEC. COMMUN. IN 'COLLECTION CZECHOSLOV. CHEM. COMMUN.,PRAGUE,VOL.27,PP.2273-2283(1962).

BIBLIOGRAPHY (CONTINUED)

FL-001	H. FLOOD, O.J. KLEPPA. J. AMER. CHEM. SOC. VOL. 69, PP. 998-1002 (1947) .
FR-001	FRICKE AND DONGES, Z. ANORG. CHEM., VOL. 250, P. 202 (1942).
GO-001	W. D. GOOD, J. PHYS. CHEM., VOL. 66, P. 380 (1962).
GR-001	R. C. GRIFFIS, J. ELECTROCHEM. SOC., VOL. 106, P. 418 (1959).
HE-001	L. G. HEPLER, R. L. GRAHAM J. AMER. CHEM. SOC. VOL. 80, PP. 3538-40 (1958).
HE-002	L.G.HEPLER, R.N.GOLDBERG, CHEM. REVIEWS, VOL. 68, PP. 229-52(1968).
HE-003	L. G. HEPLER, C. N. MULDROW, J. PHYS. CHEM., VOL.62, P. 982 (1958).
HI-001	C. HIRAYAMA, J. CHEM. ENG. DATA, VOL. 9, P. 65 (1964).
HU-001	E.J. HUBER, C.E. HOLLEY, J. AM. CHEM. SOC., VOL. 75, P. 3594, (1953).
HU-002	G.L. HUMPHREY, J. AM. CHEM. SOC., VOL. 76, P. 978 (1954).
HU-003	E. J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 793 (1963).
HU-004	E.J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 1731 (1963).
HU-006	E.J. HUBER, C. HOLLEY, J. CHEM. ENG. DATA, VOL. 13, P. 252 (1968).

HU-007 G. L. HUMPHREY, J. AM. CHEM. SOC., VOL. 75, P. 2806 (1953).

HU-008 E.J. HUBER, C. HOLLEY, J. AM. CHEM. SOC., VOL. 77, P. 1444 (1955).

IN-001 T.R. INGRAHAM, TRANS. MET. SOC. AIME VOL. 227 PP.1419-26(1963). SEE TR-005 AND TR-006

IN-002 T.R. INGRAHAM, TRANS. MET. SOC. AIME VOL. 233, PP,359-63(1965). SEE TR-005 AND TR-006

JA-001 JANAF THERMOCHEMICAL TABLES,THE DOW CHEMICAL CO.,MIDLAND,MICHIGAN, AUG.,1965.

JE-001 K. JELLINEK, J. ZAKOWSKII, Z. ANORG. CHEM., VOL. 142, PP.1-53, (1925).

JO-001 H.L. JOHNSTON, ET. AL., J. AM. CHEM. SOC., VOL. 73, P. 1112, (1951).

JU-001 JUZA AND MEYER, Z. ANORG. CHEM., VOL. 213, P. 273 (1933).

KA-001 KAPUSTINSKII AND GOLUTWIN, IZVEST, AKAD. NAUK SSSR, OTDEL KHIM. NAUK, P. 192 (1951).

KA-003 A. F. KAPUSTINSKII, O. SAMOILOV, IZV. AKAD. NAUK SSSR, OTD. KHIM. NAUK, P. 337-43 (1950). CHEM. ABSTRACTS,44:9790F.

KE-001 K.K. KELLEY. CALCULATION OF THERMOCHEMICAL PROPERTIES IN 'JANAF THERMOCHEMICAL TABLES,DOW CHEM. CO.,MIDLAND,MICH.,AUG.,1965.

KE-002 K.K. KELLEY. CONTRIBUTIONS TO DATA ON THEORETICAL METALLURGY U. S. BUREAU OF MINES, BULLETIN 584(1960).

KE-003 H.H. KELLOG. TRANS. MET. SOC. AIME VOL. 218, PP. 70-81 (1960). SEE TR-005.

BIBLIOGRAPHY (CONTINUED)

KE-004 K. K. KELLEY, W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 5984 (1962).

KE-005 K. K. KELLEY, CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY, U.S. BUREAU OF MINES BULLETIN 406, (1937).

KE-008 K. K. KELLEY, THE ENTROPIES OF INORGANIC SUBSTANCES: REVISION OF DATA, U. S. BUREAU OF MINES BULL. 477(1950).

KI-001 W. A. KIREJEW, J. CHIM. GEN. (USSR), VOL. 16, P. 1569, (1946).

KI-002 E. G. KING, W. W. WELLER, U. S. BUR. MINES, REPT. OF INVEST. NO. 5791 (1961).

KL-001 KLEMM AND SCHNICK, Z. ANORG. CHEM., VOL. 226, P. 353 (1936).

KO-001 KORSHUNOV, J. PHYS. CHEM.(U.S.S.R.), VOL. 13, P. 703 (1939).

KR-001 O. H. KRIKORIAN, J. PHYS. CHEM., VOL. 67, PP. 1586-9 (1963).

KR-002 KRAUS AND RIDDERHOFF, J. AM. CHEM. SOC., VOL. 56, P. 79 (1934).

KU-001 O. KUBASCHEWSKI, ET AL . METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS 4TH EDITION (1967).

KU-002 O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS, (1959).

KU-003 O. KUBASCHEWSKI , THERMO. DATA OF THE ALLOYS, PERGAMON PRESS, (1956).

KU-004 KUBASCHEWSKI AND WEIBKE, THERMOCHEMIE DER LEGIERINGEN, SPRINGER, BERLIN, 1943.

BIBLIOGRAPHY (CONTINUED)

KU-005 O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS, (1951).

LA-001 KALORISCHE ZUSTANDSGROESSEN IN 'LANDOLT BOERNSTEIN', SPRINGER-VERLAG, BERLIN,VOL.2,PART4(1961).

LA-002 W. LATIMER, J. AM. CHEM. SOC., VOL. 73, P. 1480 (1951).

LE-003 LEVITSKII, ET AL., RUSS. J. PHYS. CHEM., VOL. 35, NO. 6, P. 671 (1961)

MA-001 P. G.MASLOV. THERMODYNAM. CHARACTERISTICS OF CALCIUM, GALLIUM, INDIUM, AND THALLIUM COMPOUNDS. ZHUR. OBSCHCEIKHIM.,VOL.29,PP.1413-1423(1959).

MA-002 A. D. MAH, J. AM. CHEM. SOC., VOL. 81, P. 1582 (1959).

MA-003 A.D. MAH, U. S. BUR. MINES, REPORT OF INVESTIGATIONS NO. 5965, (1962).

MA-005 MARCHAL, J. CHIM. PHYS., VOL. 23, P. 38, (1926).

ME-001 G. MEYER, E.H.P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 670, (1962).

ME-003 G. MEYER, E. H. P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 495 (1962).

MI-001 MIXTER, AM. J. SCI. , VOL. 28, P. 103 (1909).

MO-001 M. P. MOROZOVA, L. GETSKINA, VESTNIK LENINGRAD. UNIV., VOL. [illegible] NO. 22, SER. FIZ. I KHIM. NO. 4, VOL. 128, (1959).

MO-002 A. N. MOROZOVA, N. A. NOVOKHATSKII, IZV. A N SSSR, [illegible] N., METALLURGIYA I TOPLIVO, NO. 6, P. 3 (1962).

NB-001 SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART I,NATIONAL BUREAU OF STANDARDS,1965.

NB-002 SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART II,NATIONAL BUREAU OF STANDARDS,1966.

NB-003 F,ROSSINI,ET AL. SELECTED VALUES OF CHEM. THERM. PROPERTIES, NATL. BUREAU OF STANDARDS, CIRCULAR 500, (1952).

NB-004 NATIONAL STANDARD REFERENCE DATA SERIES NBS-7. HIGH TEMPERATURE PROPERTIES AND DECOMPOSITION OF INORGANIC SALTS. PART I SULFATES.

NB-005 SELECTED VALUES OF CHEM. THERM. PROPS., NATNL. BUR. STDS., TABLES FOR FIRST 34 ELEMENTS IN STD. ORDER OF ARRANGEMENT. TN 270-3 (1968).

OR-001 M.H. ORTNER, J. CHEM. PHYS., VOL. 34, P. 556 (1961).

OW-001 B. OWENS, S. W. MAYER, J. INORG. NUCL. CHEM., VOL. 26, P. 501, (1964). SEE TR-005, TR-006.

OW-002 OWEN, J. AM. CHEM. SOC., VOL. 56, P. 1695 (1934).

PA-001 N.PARRAVANO, G.MALQUORI, ATTI. R. ACAD. LINCEI. SER. 6, VOL. 7, P. 189 (1928).

PA-002 PARRAVANO AND MALQUORI, ATTI. REND. ACCAD. LINCEI, SER. 6, VOL. 7, P. 109 (1928).

PE-001 J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).

RE-001 A. REISMAN, J. AMER. CHEM. SOC., VOL. 80, PP.3558-9 (1958).

RE-002 L.A. REZNITSKII, ZH. FIZ. KHIM., VOL. 38, P. 760 (1964).(CHEMICAL ABSTRACTS,61:8004F.)

BIBLIOGRAPHY (CONTINUED)

RE-003	RENEGADE AND CONSTEANU, BULL. SOC. CHIM. FRANCE, VOL. 15, P. 717 (1914).
RE-005	RENEGADE AND CONSTEANU, COMPT. REND., VOL. 158, P. 946 (1914).
RO-001	W. ROTH, Z. ELEKTROCHEM., VOL. 46, P. 42 (1940).
RO-002	W.ROTH, ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA,XI, SECT. 12, 'THERMOCHEMISTRY (1931-1934),' HERMANN AND CO., PARIS, (1937).
RO-003	W. ROTH, G. BECKER, Z. PHYSIK. CHEM., VOL. A159, P. 1 (1932).
RO-004	T. ROSENQVIST, J. IRON AND STEEL INSTITUTE, VOL. 176, P. 36, (1954).
RO-005	W.A. ROTH, F I A T REPORTS OF GERMAN SCIENCE, INORG. CHEM., VOL. 4, P. 214 (1948).
RO-006	ROSSINI AND BICHOWSKY, THERMOCHEMISTRY OF CHEMICAL SUBSTANCES, NEW YORK (1936).
SA-001	P. SABATIER, ANN. CHIM. PHYS., VOL. 22, P.5 (1881).
SC-001	H. SCHAEFER, H. HEITLAND, Z. ANORG. CHEM., VOL. 304, P. 249, (1960).
SC-002	N. G. SCHMALL, E. MINZL, Z. PHYSIK. CHEM. (FRANKFURT), VOL. 47, P. 142 (1965).
SC-003	R. SCHENCK, P.VON DER FORST, Z. ANORG. CHEM., VOL. 241, PP. 145-57, (1939).
SC-004	SCHENCK AND RAUB, Z. ANORG. CHEM., VOL. 178, P. 225 (1929).

BIBLIOGRAPHY (CONTINUED)

SH-001 C. SHOMATE, J. AM. CHEM. SOC., VOL. 68, PP. 964-6 (1946).

SH-002 SHOMATE, NAYLOR, AND BOERICKE, U. S. BUR. MINES, REPT. INVEST. NO. 3864 (1946), J. AM. CHEM. SOC., VOL. 68, P. 1003 (1946).

SI-001 SIMON AND THALER, Z. ANORG. CHEM., VOL. 162, P. 253 (1927).

ST-001 J.R. STUBBLES, F.D. RICHARDSON, TRANS. FARADAY SOC., VOL. 56, P. 1460 (1960).

ST-002 R.P. STEIGER, E.D. CATER, J. PHYS. CHEM., VOL. 72, PP. 2231-3(1968).

SU-001 K. SUDO, SCIENCE REPT. RESEARCH INST. TOHOKU UNIV., SER.A, VOL. 2, P. 507 (1950).

TA-001 M. TAGAMI, W. BELL, J. PHYS. CHEM., VOL. 70, P. 3735 (1960).

TH-001 THOMSEN, THERMOCHEMISCHE UNTERSUCHUNGEN, BARTH, LEIPZIG (1882-1886).

TR-001 TRACOR VALUE ESTIMATED USING MODIFIED KOPP'S RULE, SEE TECHNICAL MEMORANDA 004-009-CH4 AND 004-009-CH13A

TR-002 TRACOR VALUE ESTIMATED USING MODIFIED ERDOS METHOD, SEE TECHNICAL MEMORANDA 004-009-CH1 AND 004-009-CH1A.

TR-003 TRACOR VALUE ESTIMATED USING MODIFIED LATIMER METHOD, SEE TECHNICAL MEMORANDUM 004-009-CH5.

TR-004 HEAT CAPACITY OBTAINED BY SUMMING HEAT CAPACITIES OF CONSTITUENT OXIDES FROM TRACOR DATA BASE. SEE TECHNICAL MEMORANDUM 004-009-CH9.

TR-005 HEAT OF FORMATION OBTAINED BY COMBINING HEAT OF REACTION FROM LITERATURE WITH HEATS OF FORMATION FROM TRACOR DATA BASE.

BIBLIOGRAPHY (CONTINUED)

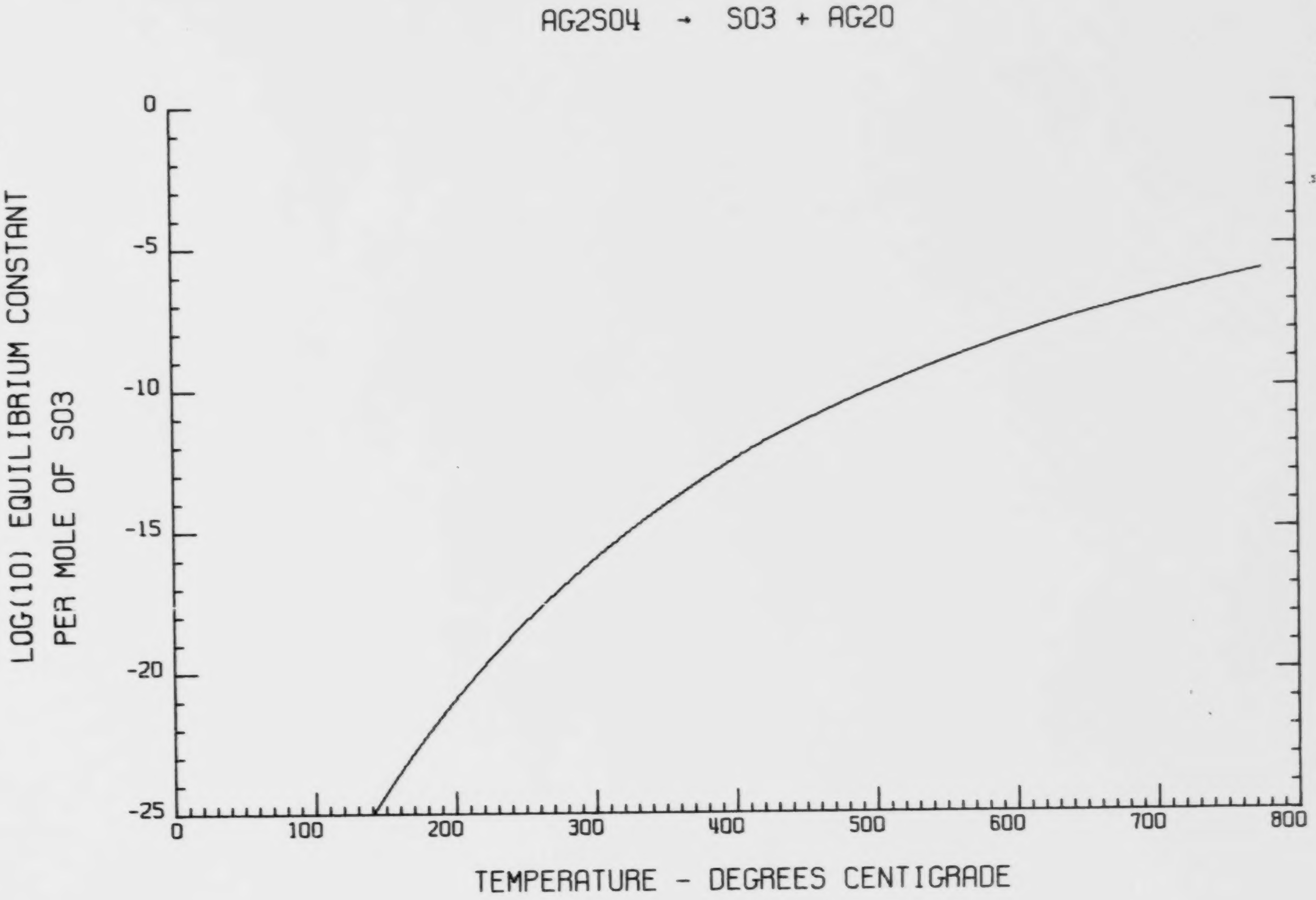
TR-006	ABSOLUTE ENTROPY OBTAINED BY COMBINING ENTROPY OF REACTION FROM LITERATURE WITH ABSOLUTE ENTROPIES FROM TRACOR DATA BASE.
TR-007	ENTROPIES FOR TUNGSTATES AND MOLYBDATES ESTIMATED FROM OBSERVATIONS BASED ON RESULTS IN TECHNICAL MEMORANDUM 004-009-CH5.
TR-008	THE HEAT CAPACITY OF CRO3 WAS ESTIMATED FROM THE HEAT CAPACITIES OF WO3 AND MOO3.
TR-009	TRACOR VALUE ESTIMATED FROM OXIDE HEAT CAPACITY. SEE TECHNICAL MEMORANDUM 004-009-CH13.
TR-010	THIS VALUE HAS BEEN SELECTED AS THE BEST OF SEVERAL DIFFERENT REPORTED VALUES. SEE TECHNICAL MEMORANDUM 004-009-CH18
VA-001	V. A. VANYUKOV, N. A. KISELEVA, YUB. SBOR. TRUD. KAFED. I LAB. TYAZH. METALL. MOSK. INST. TSVETNYKH METALL. I ZOLOTA NO. 7, P. 304, (1939).
WA-001	VON WARTENBERG. Z. ANORG. CHEM., VOL. 71, P. 427 (1911).
WA-002	J. S. WARNER, J. ELECTROCHEM. SOC., VOL. 114, P. 68 (1967).
WE-001	WESTRUM, ET AL., J. CHEM. PHYS., VOL. 35, P. 1670 (1961).
WI-001	D.E.WILCOX. METHOD FOR ESTIMATING HEAT OF FORMATION OF INORGANIC COMPOUNDS, M.S.THESIS, UNIVERSITY OF CALIF., BERKLEY, CALIF., 1962.
WI-002	WISE, ET. AL., J. PHYS. CHEM., VOL. 66, P. 381 (1962).
WO-001	WOHLER AND WITZMAN, Z. ELEKTROCHEM., VOL. 14, P. 97 (1908).
WO-002	WOHLER AND JOCKUM, Z. PHYSIK. CHEM., VOL. A167, P. 169 (1933).

BIBLIOGRAPHY (CONTINUED)

WO-003 WOHLER, ZH. FIZ. KHIM., VOL. 167, P. 176 (1933).

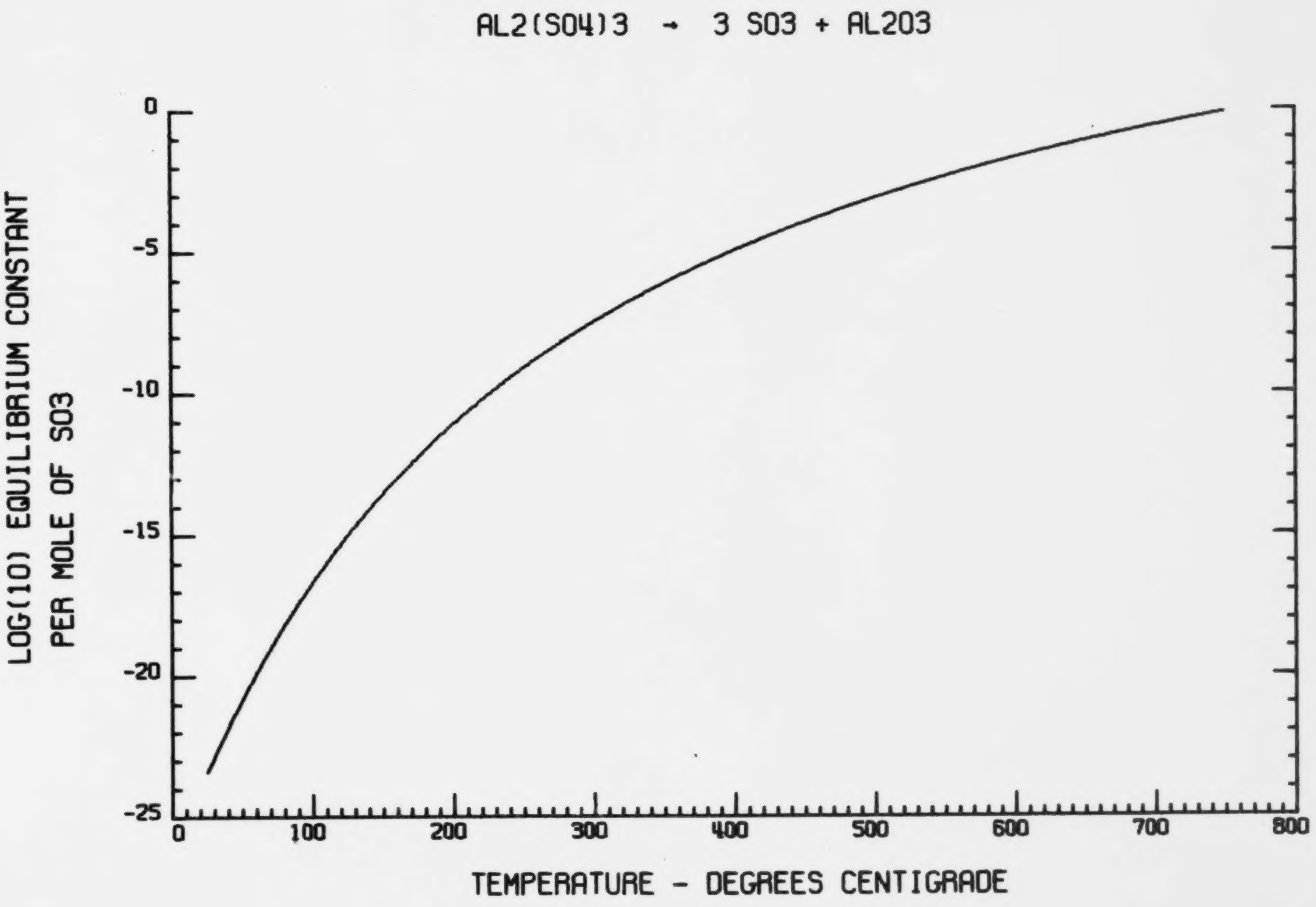
8.2 THERMODYNAMIC, KINETIC, AND ECONOMIC DATA

8.2.2 Log K Plots for Sulfate Decomposition Reactions

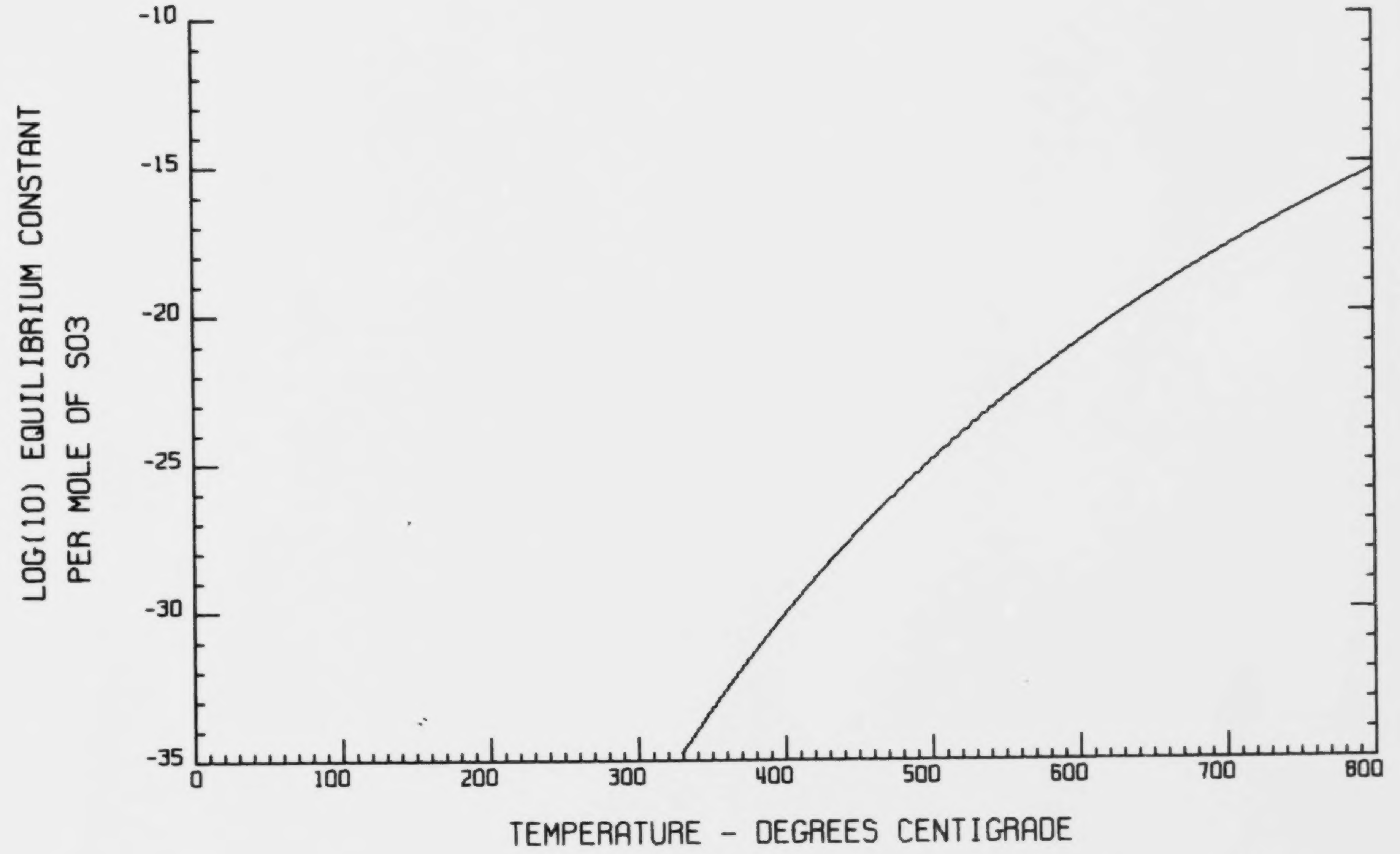


26 JUL 68

TRACOR

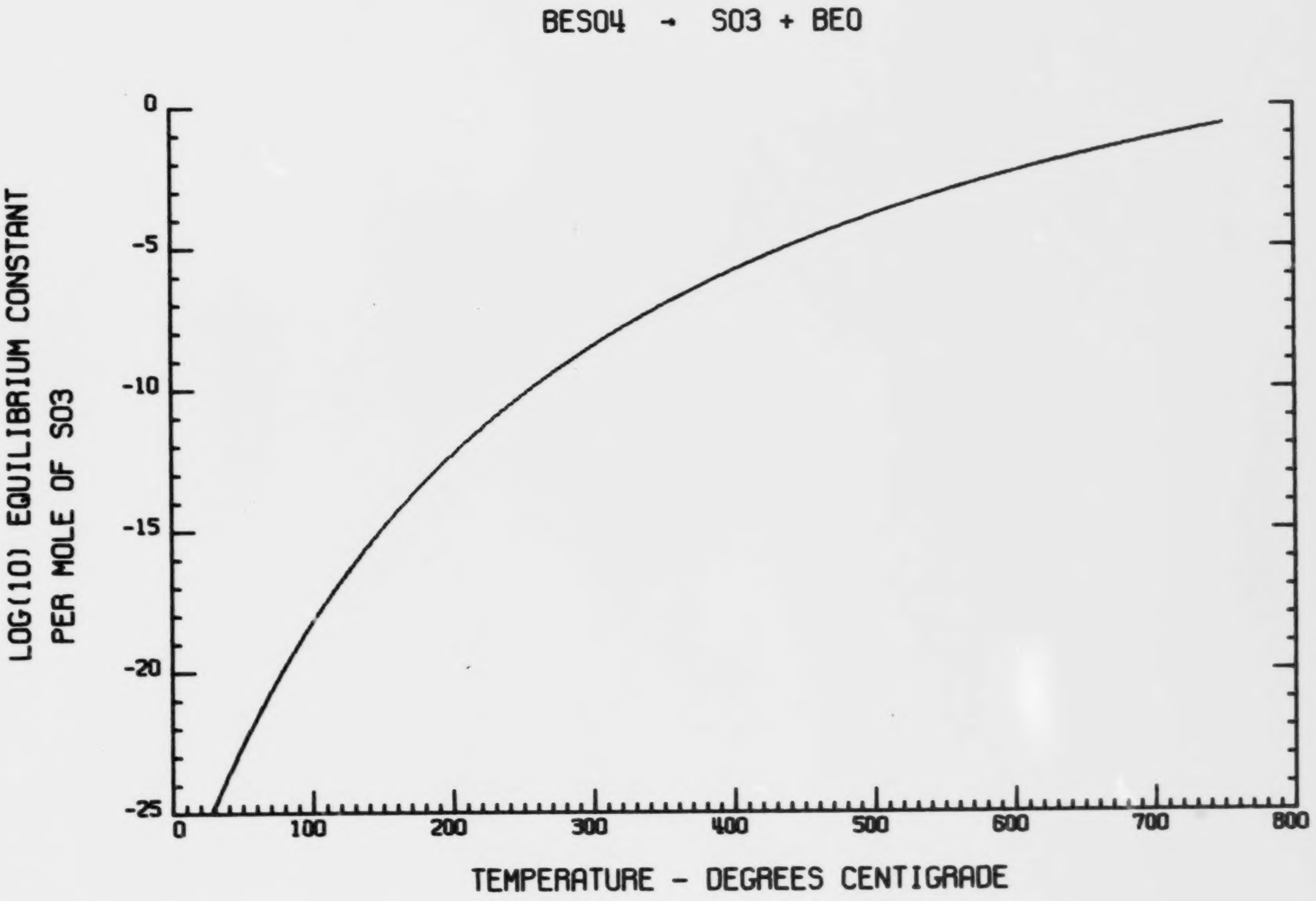

AL2(SO4)3 → 3 SO3 + AL2O3
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO3
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

11 JUL 68

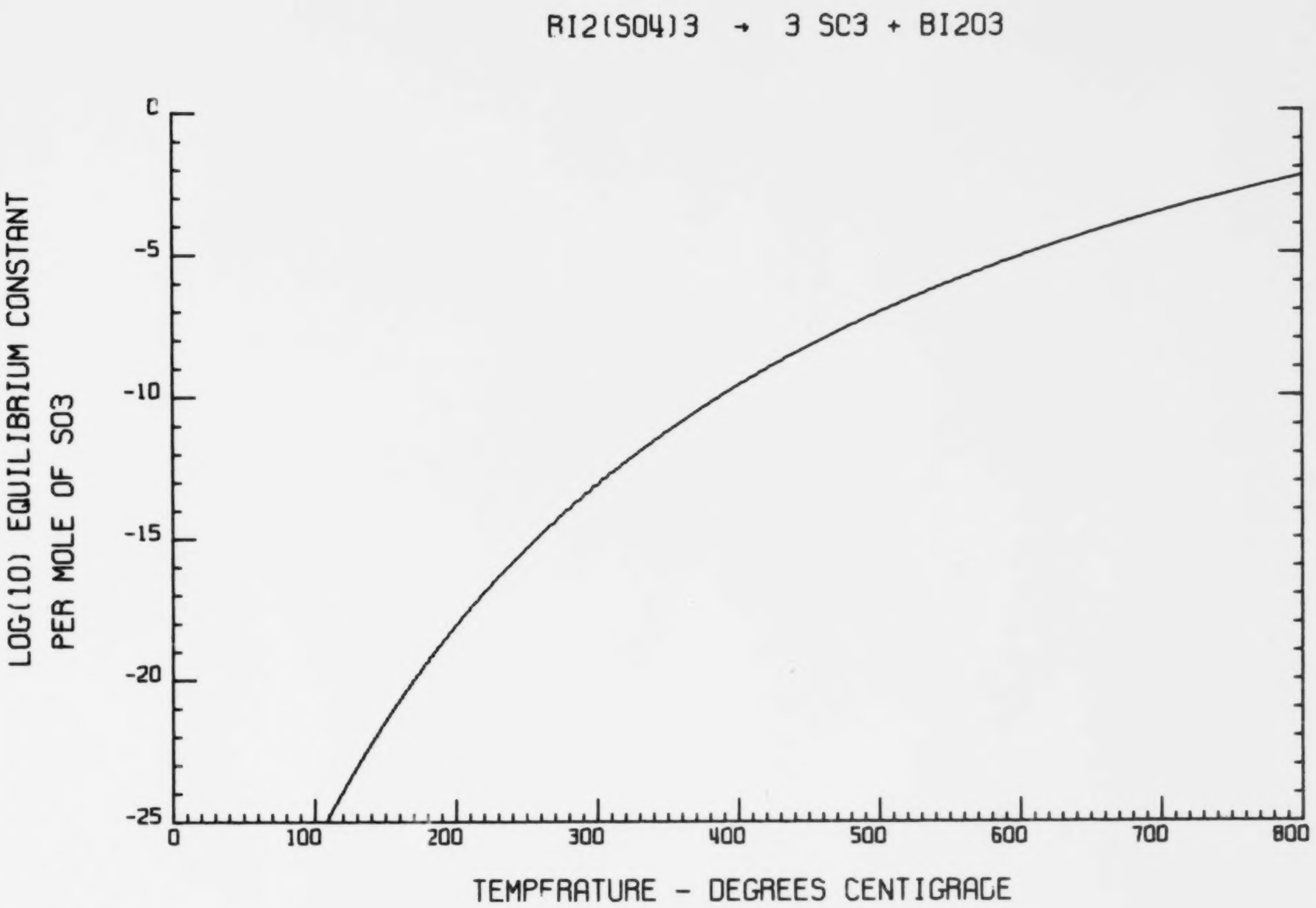


BASO4 → SO3 + BAO

21 OCT 68

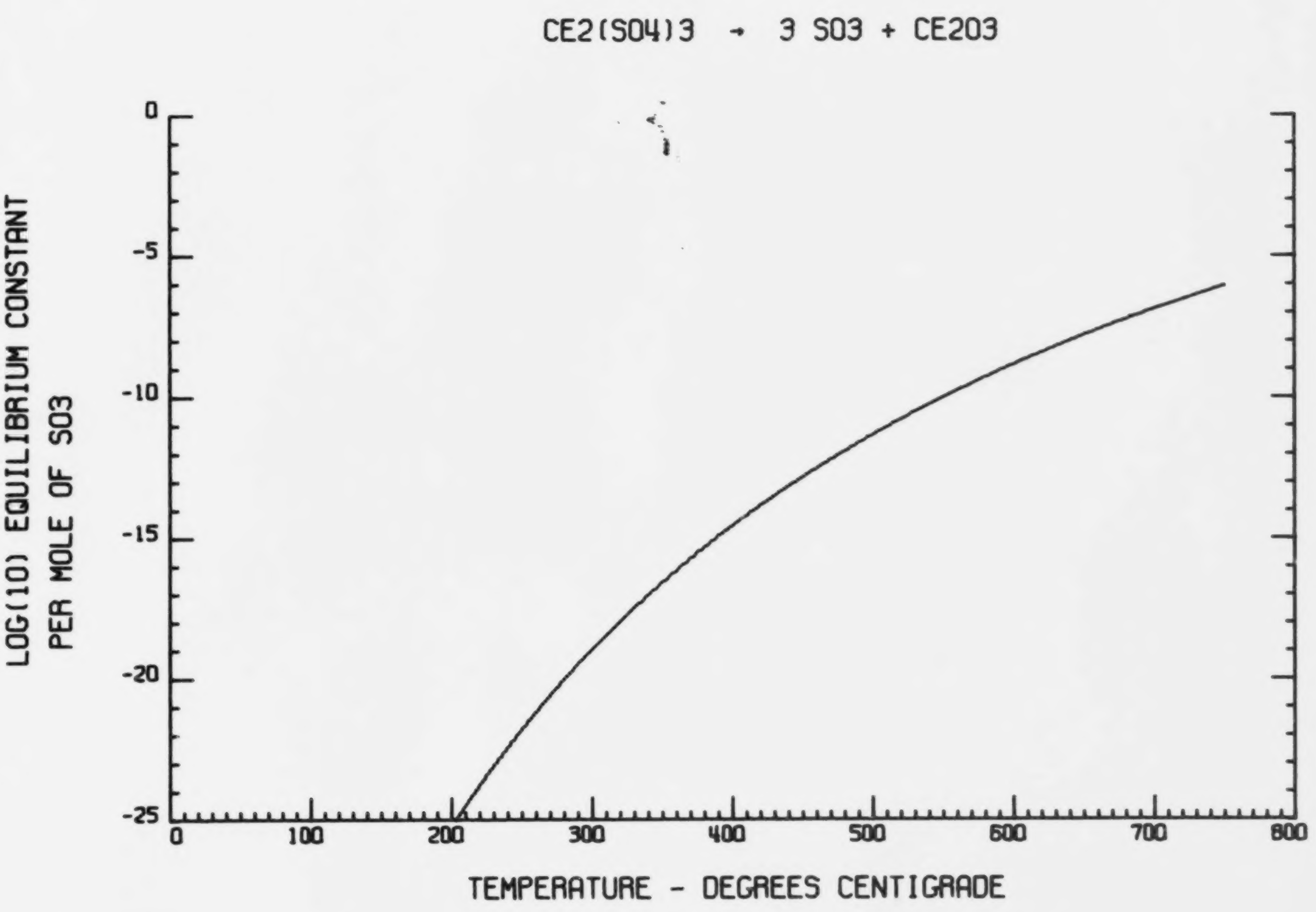

BESO4 → SO3 + BEO
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO3
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

11 JUL 68



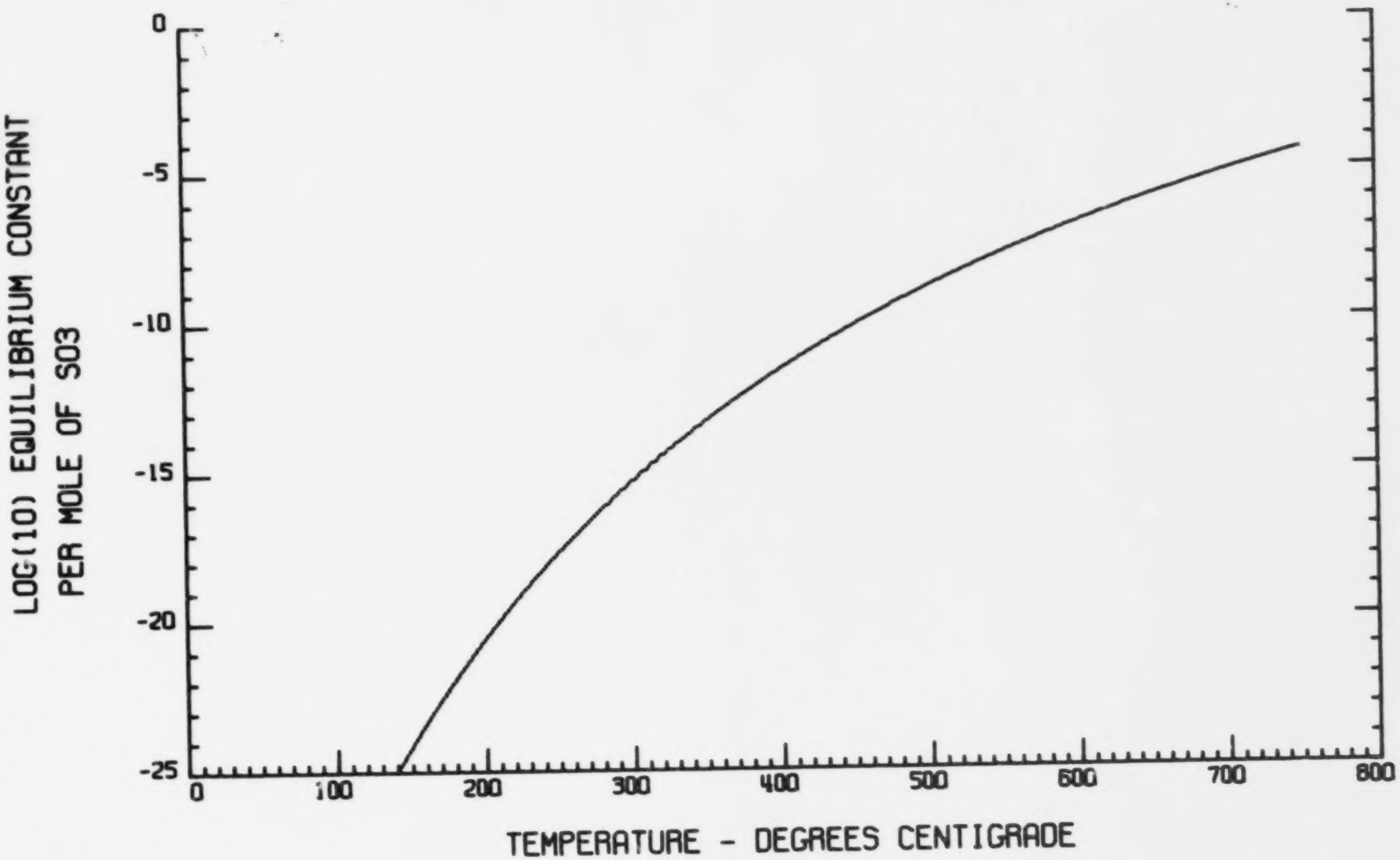
RI2(SO4)3 → 3 SC3 + BI2O3

21 OCT 68



11 JUL 68

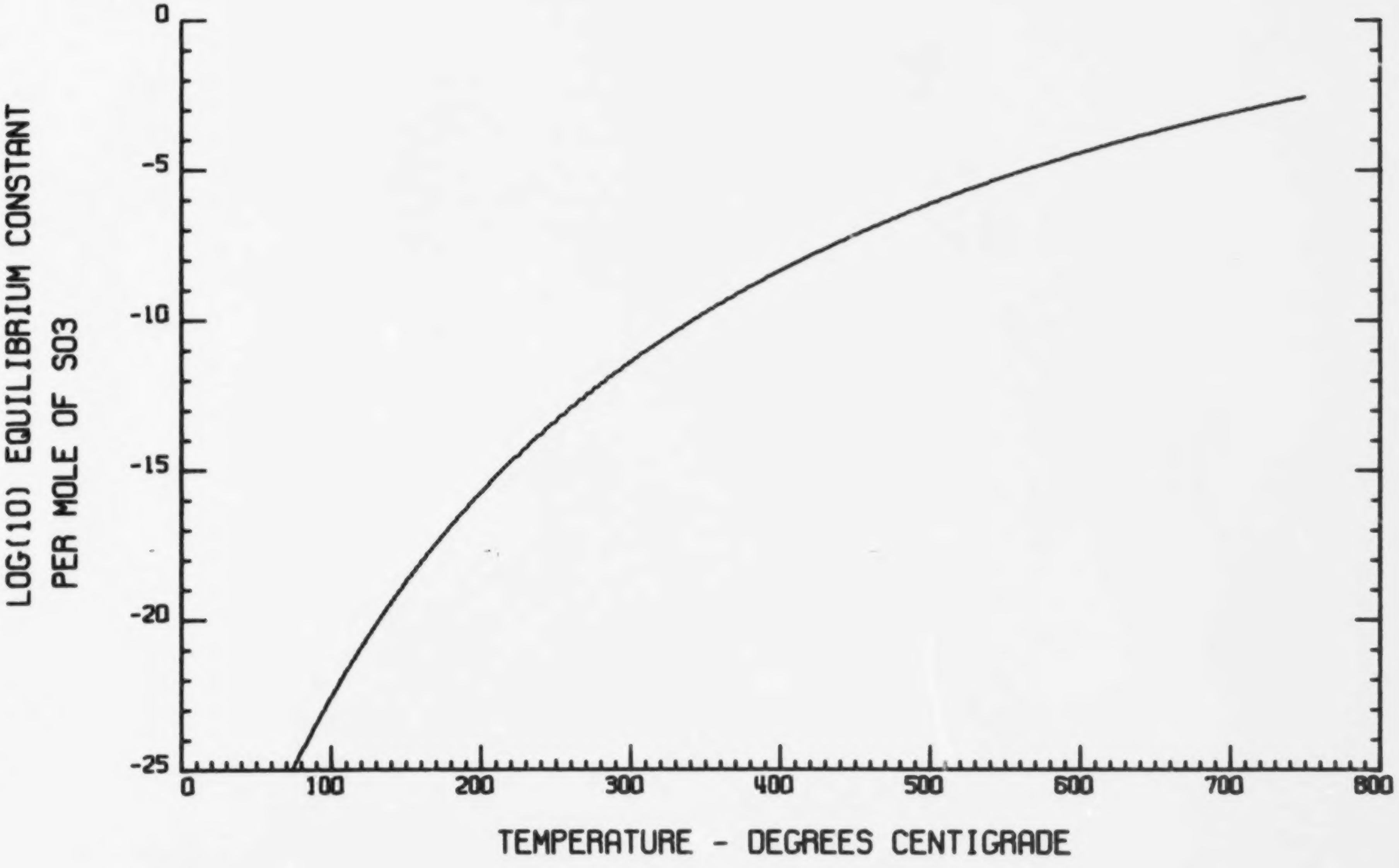
TRACOR


CDSO4 → SO3 + CDO

11 JUL 68

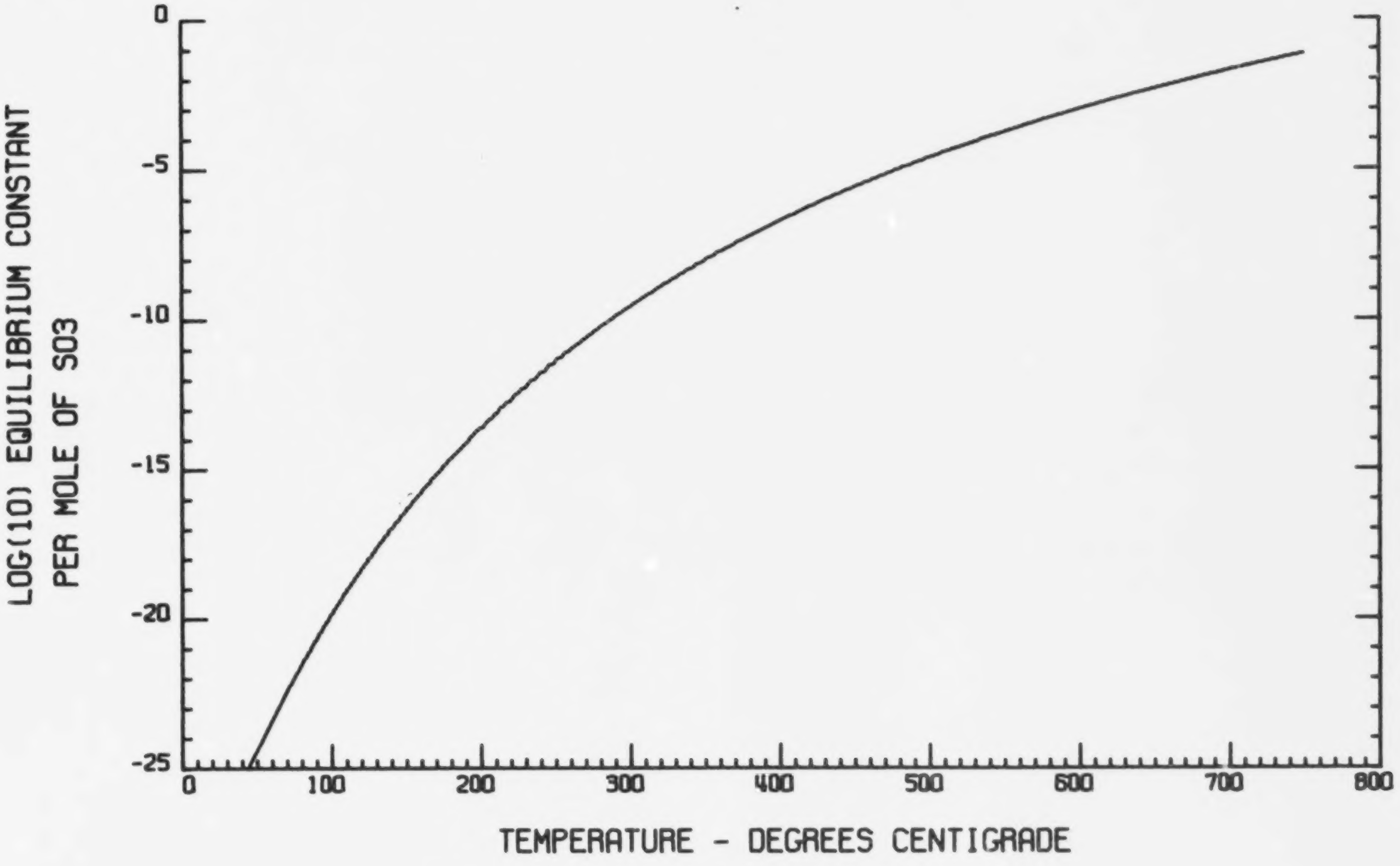
TRACOR

COSO4 → SO3 + COO



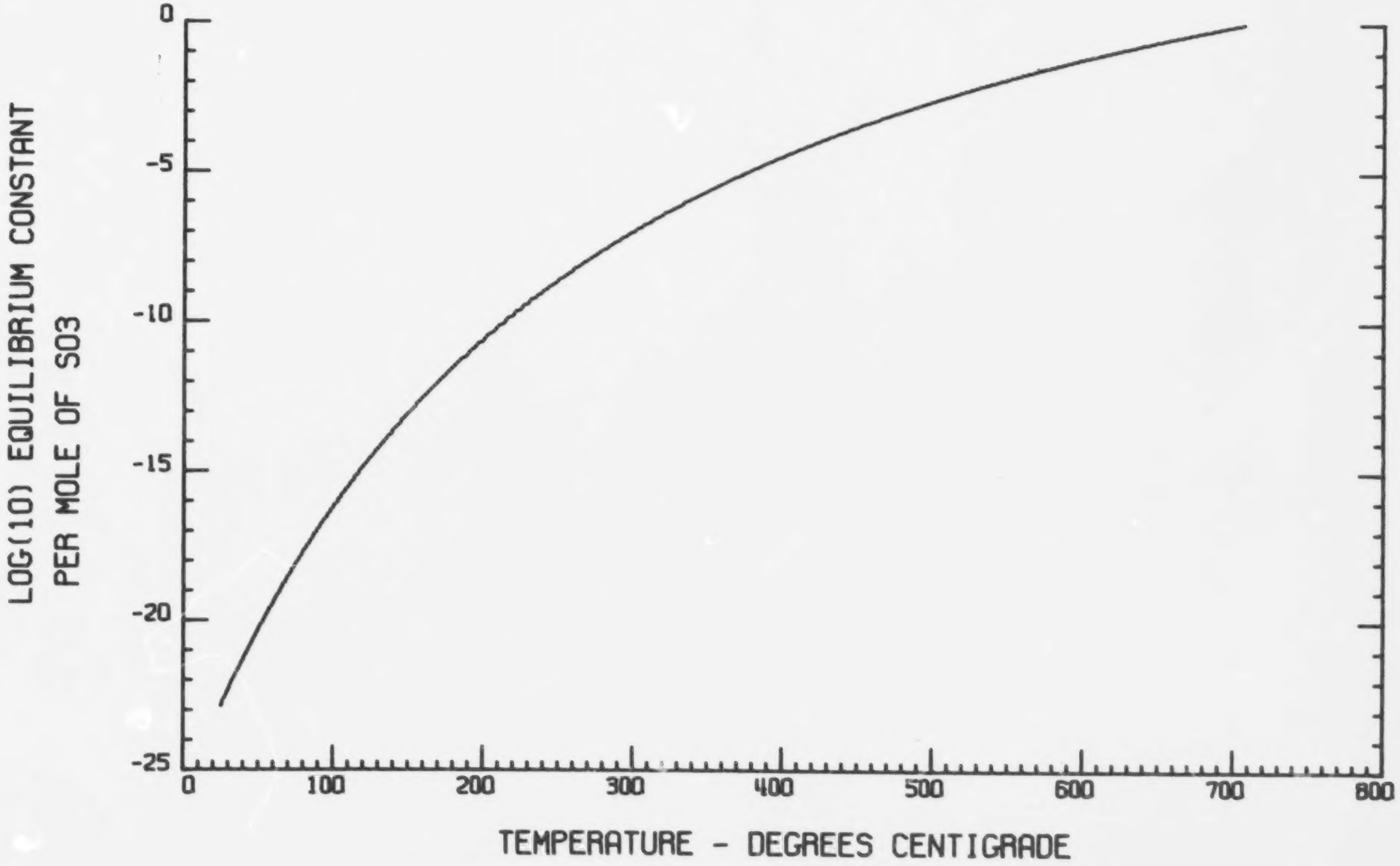
11 JUL 68

CUSO4 → SO3 + CUO



11 JUL 68

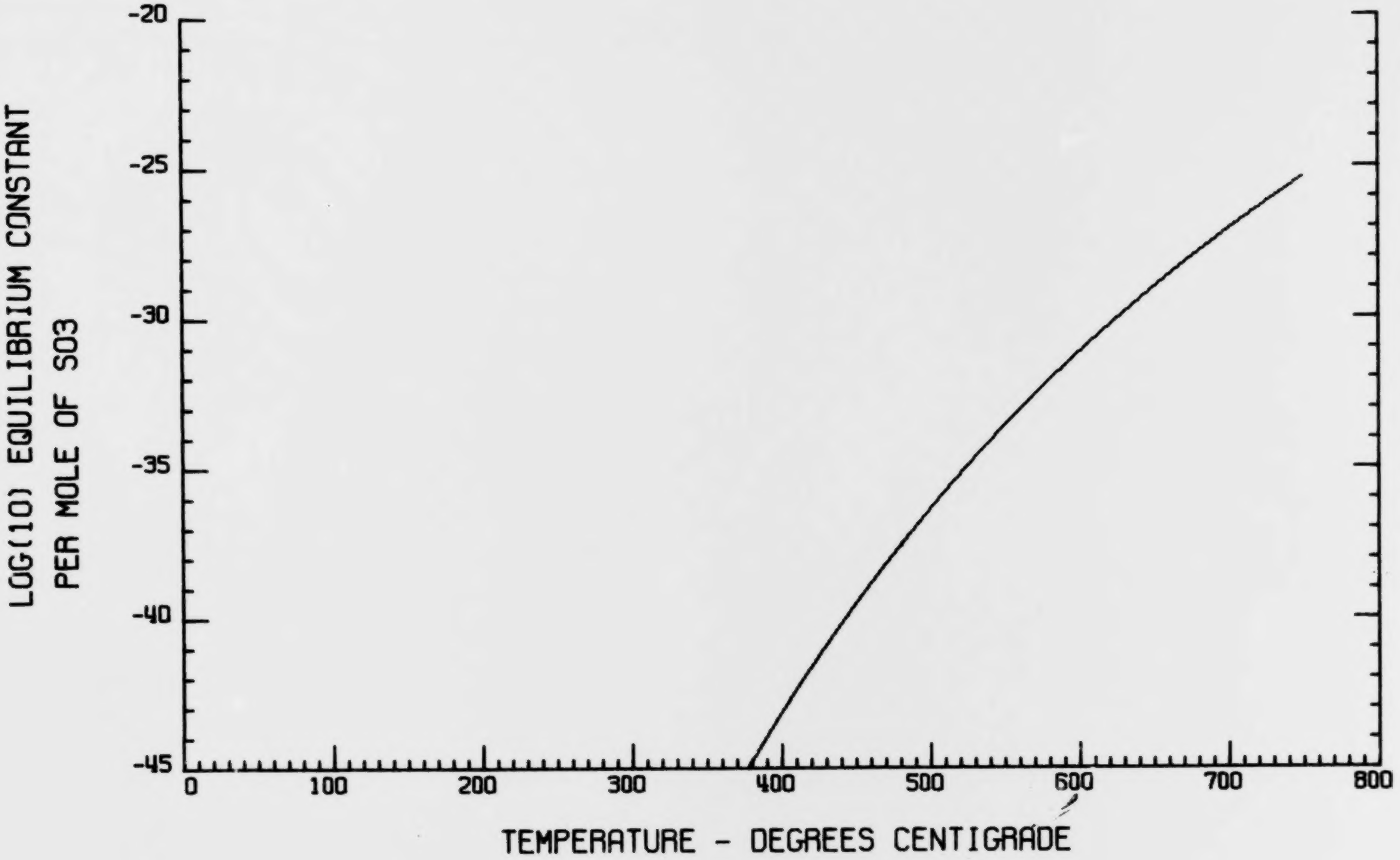
FE2(SO4)3 → 3 SO3 + FE2O3



11 JUL 68

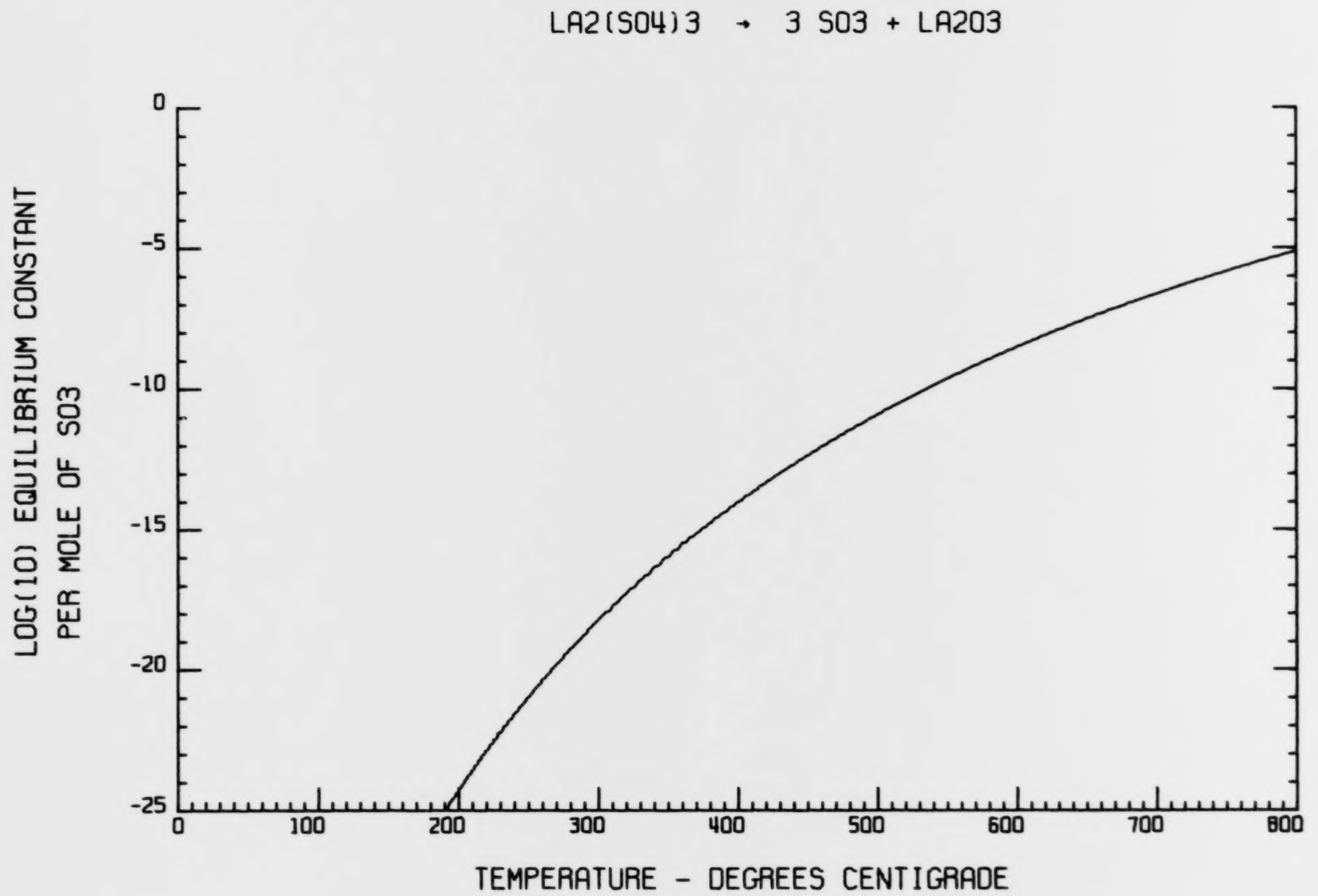
TRACOR

K2SO4 → SO3 + K2O

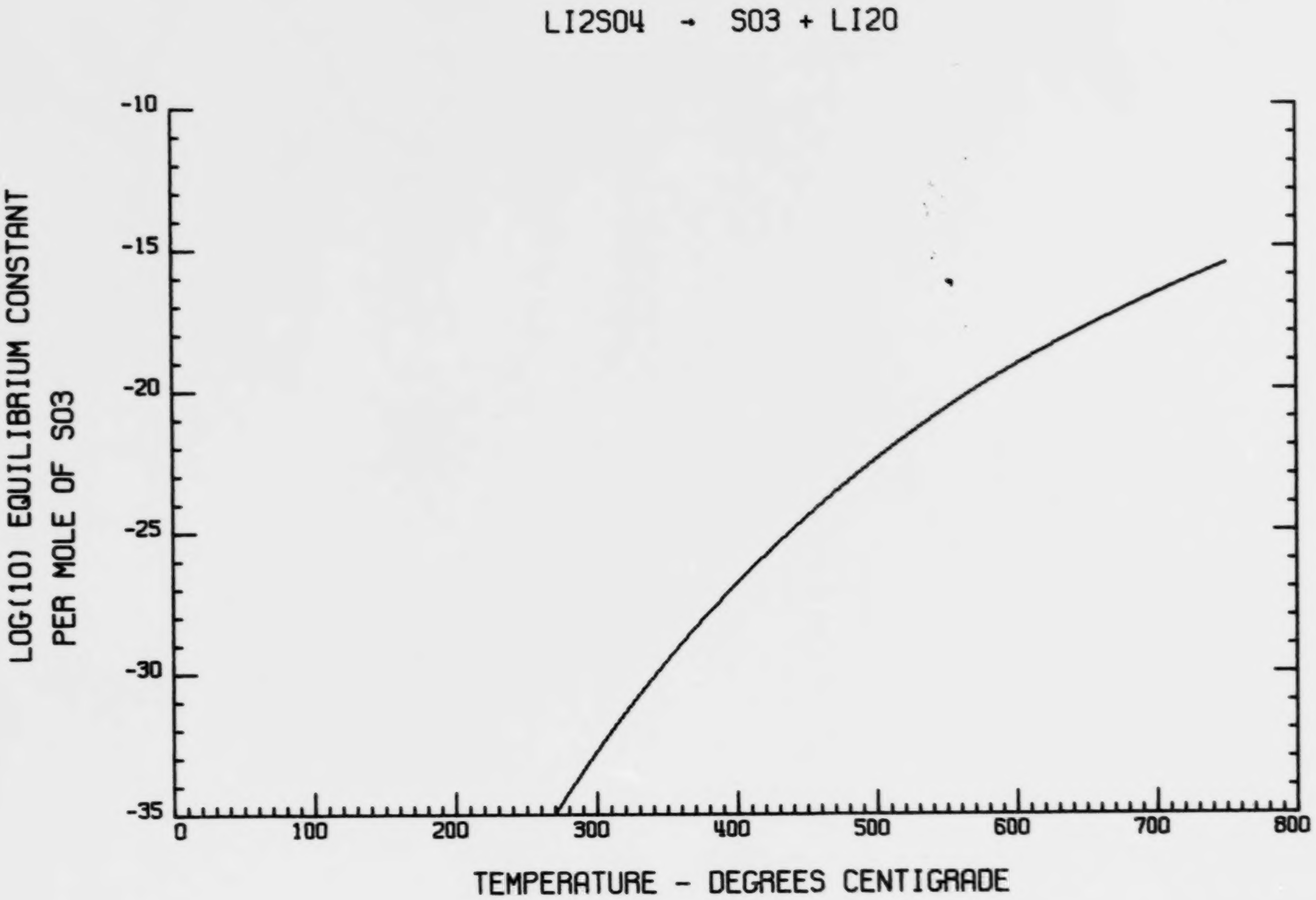


11 JUL 68

TRACOR

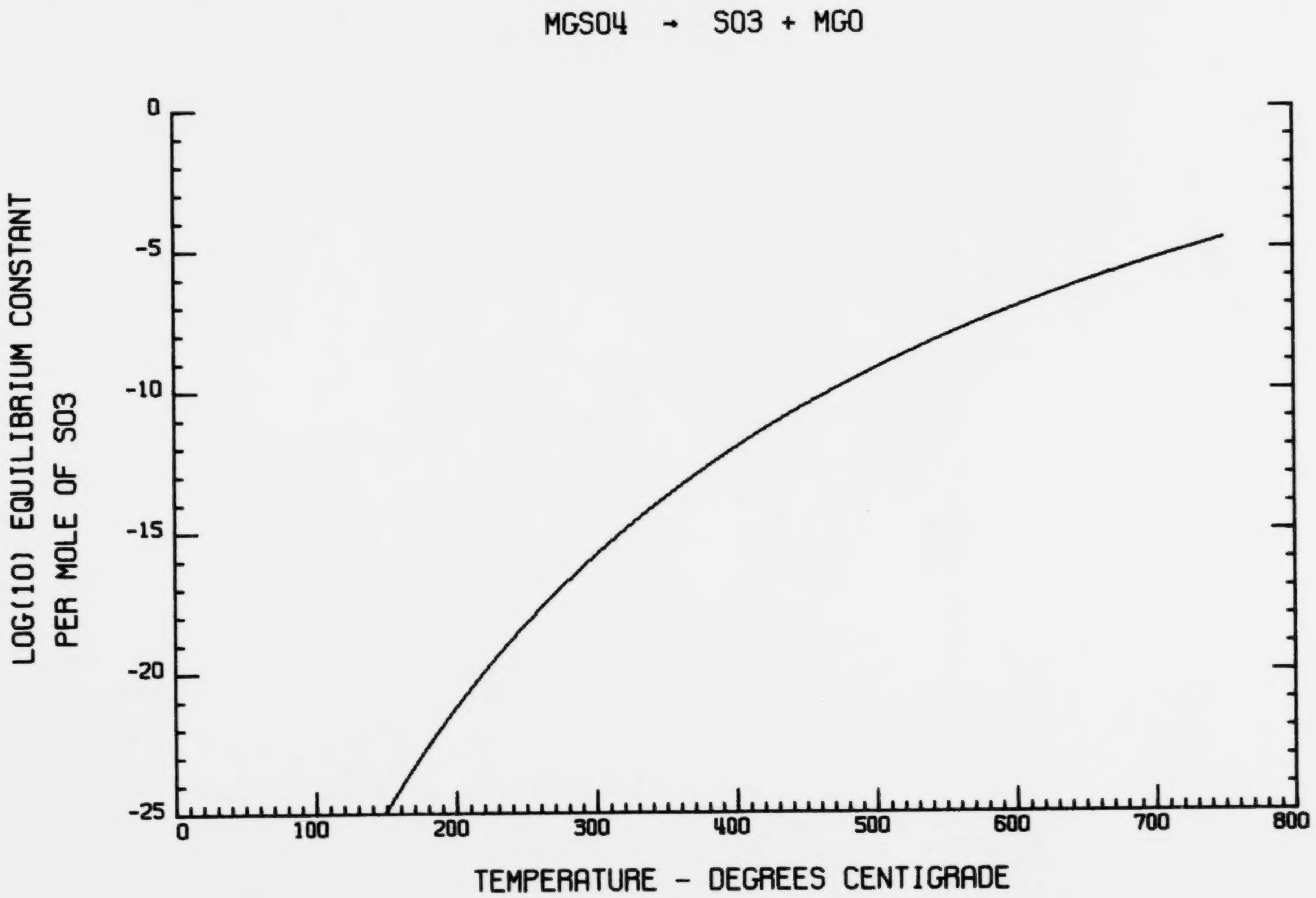

LA2(SO4)3 → 3 SO3 + LA2O3

21 OCT 68



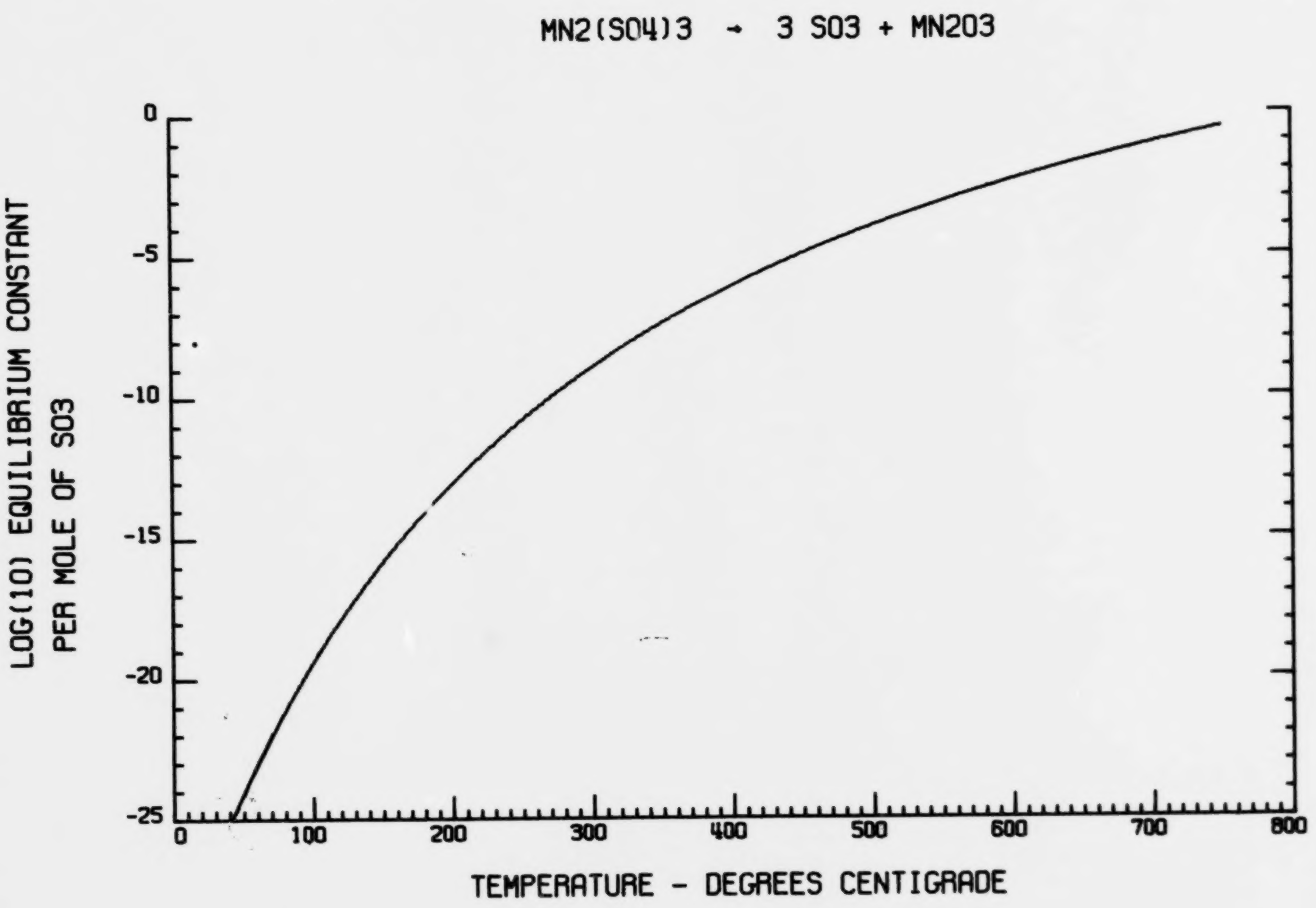
11 JUL 68

TRACOR



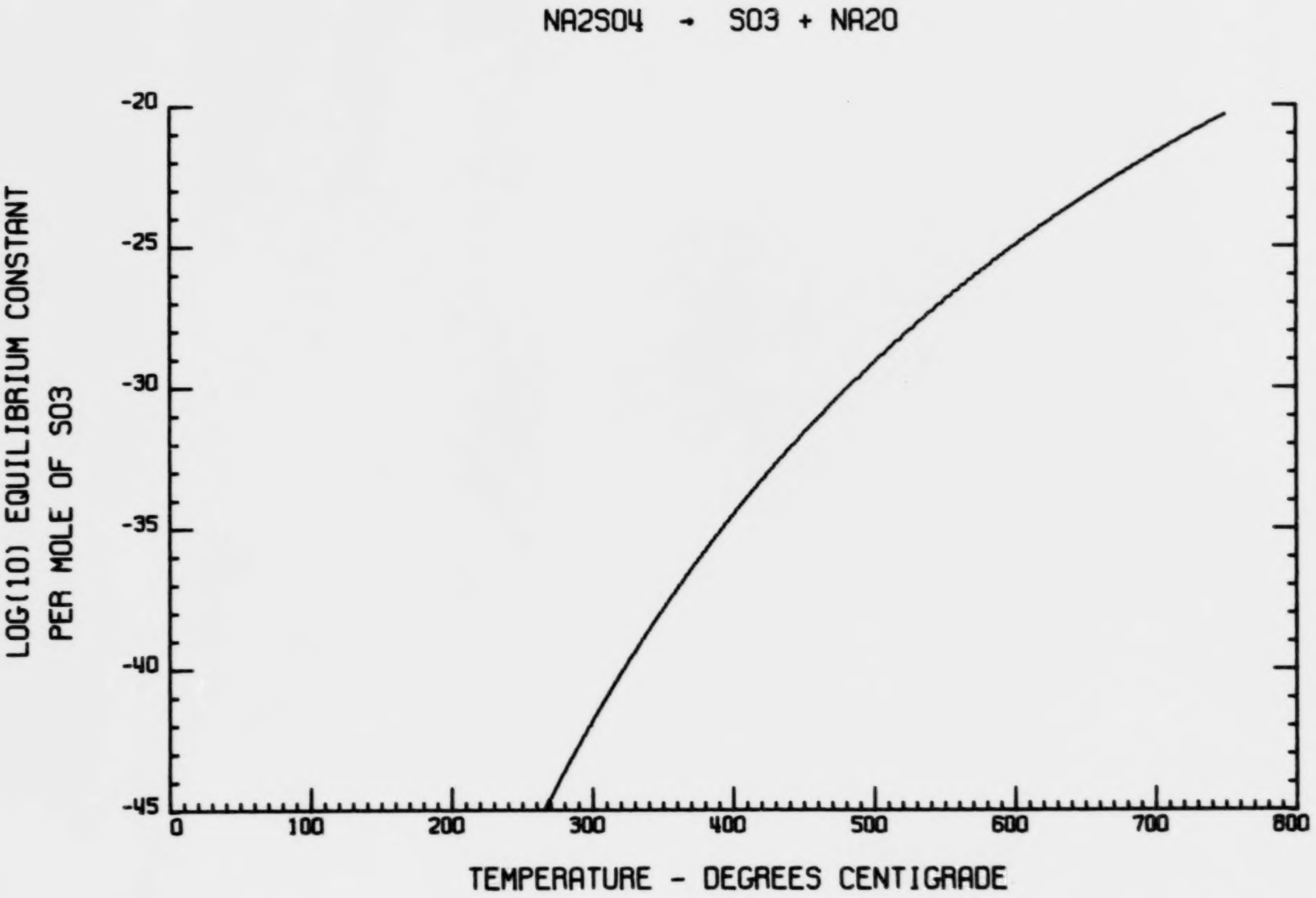
11 JUL 68

TRACOR



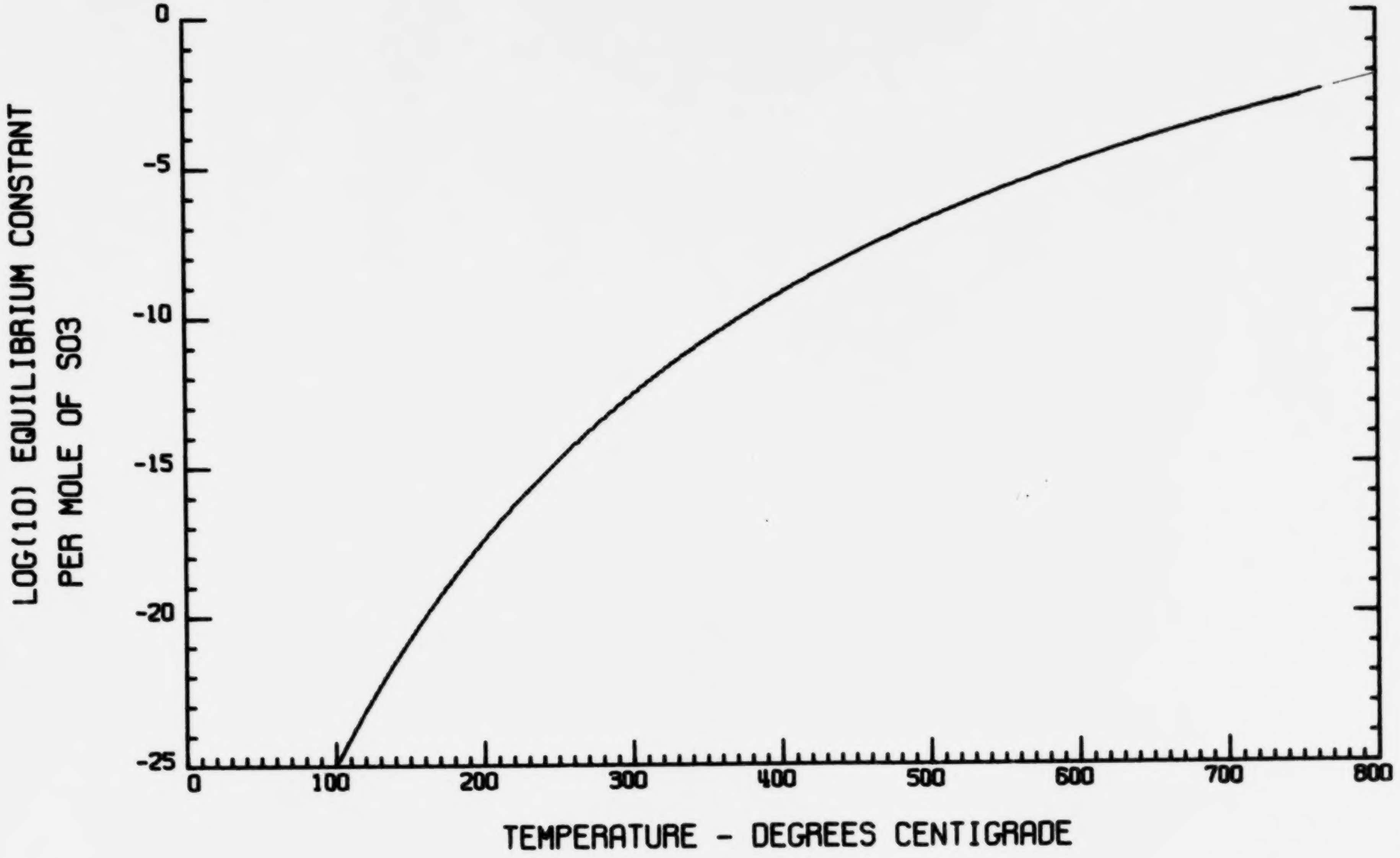
11 JUL 68

TRACOR


NA2SO4 → SO3 + NA2O
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO3
-20
-25
-30
-35
-40
-45
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

15 JUL 68

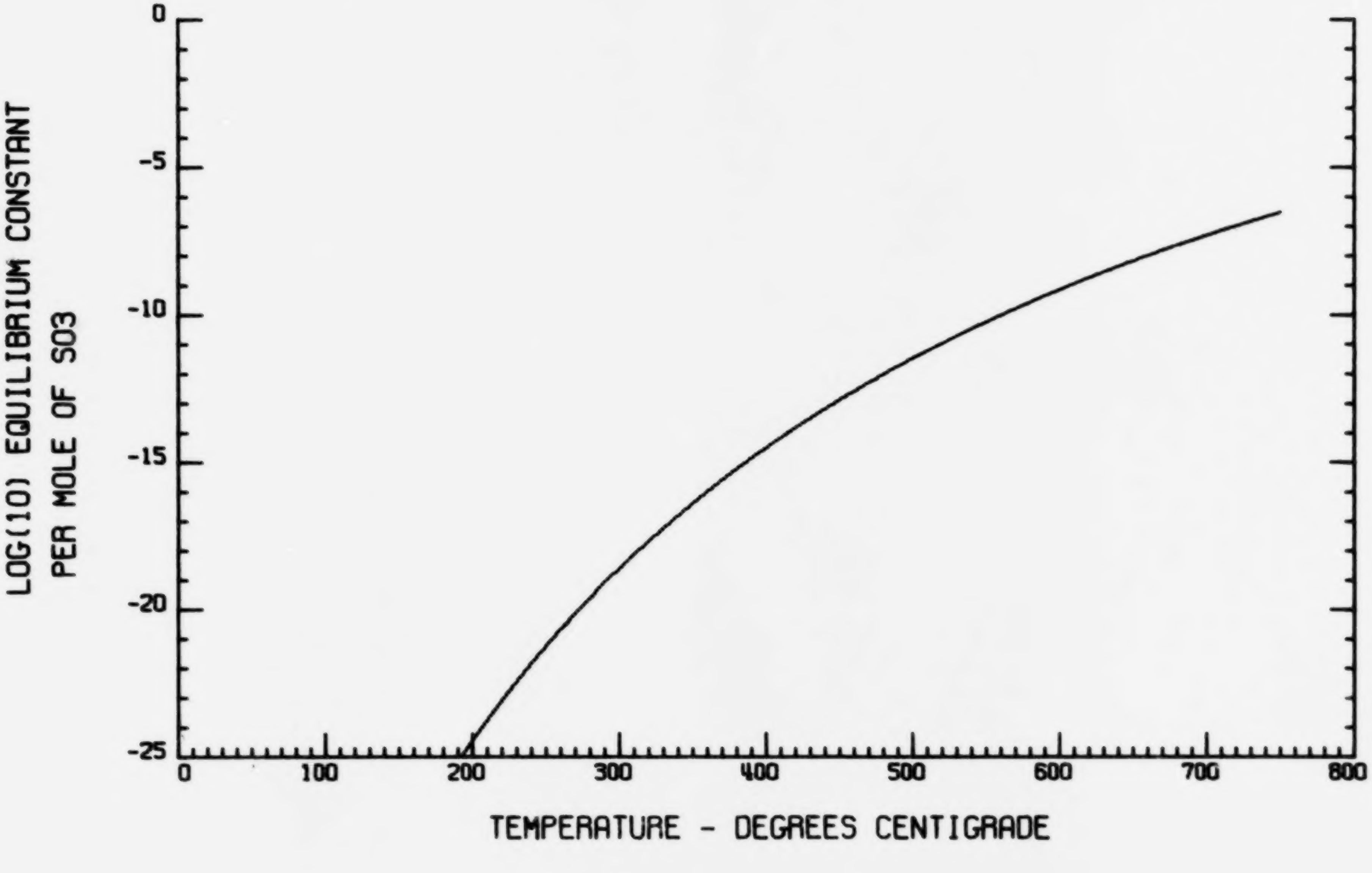
NISO4 → SO3 + NIO



11 JUL 68

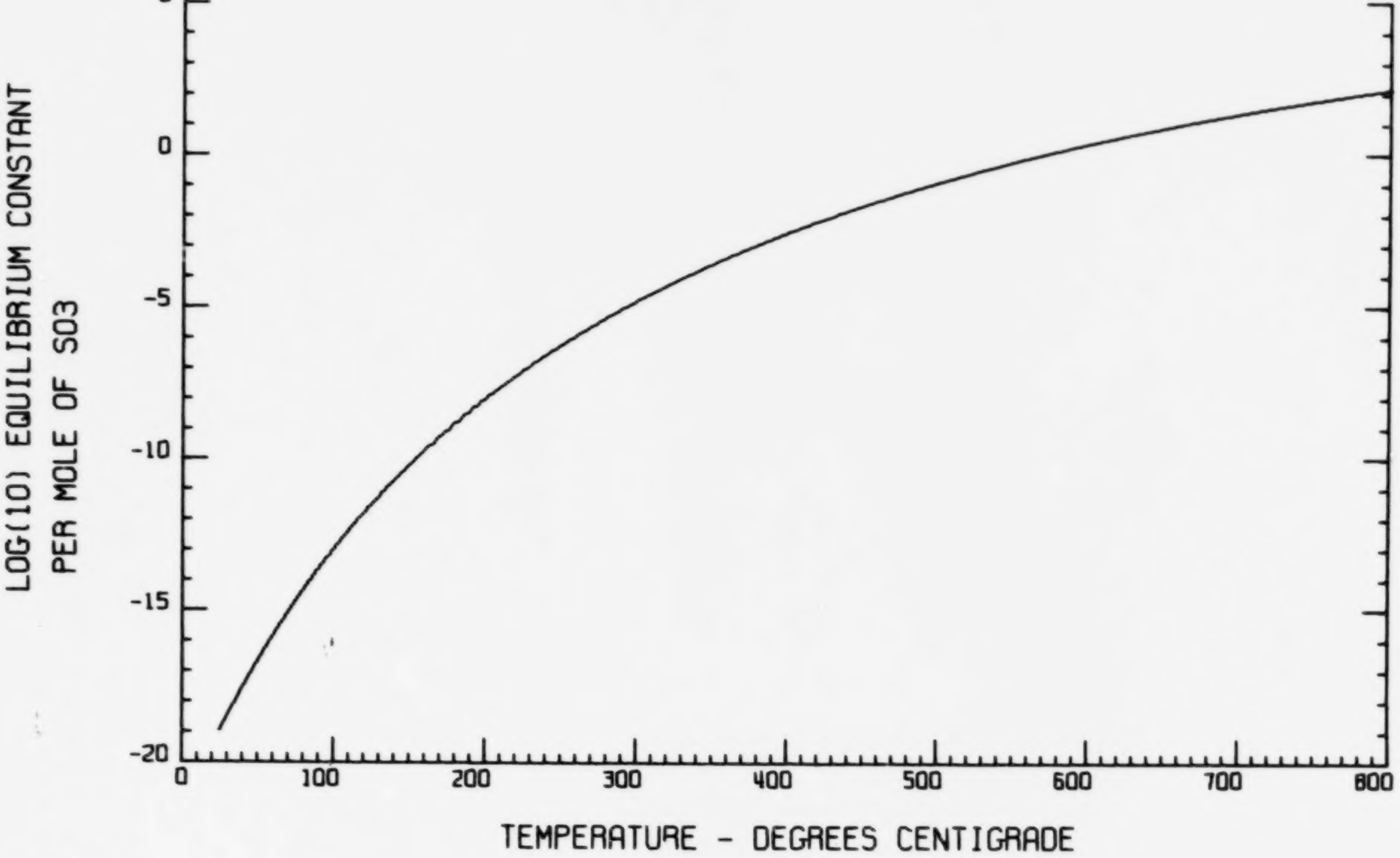
TRACOR

PBSO4 → SO3 + PBO



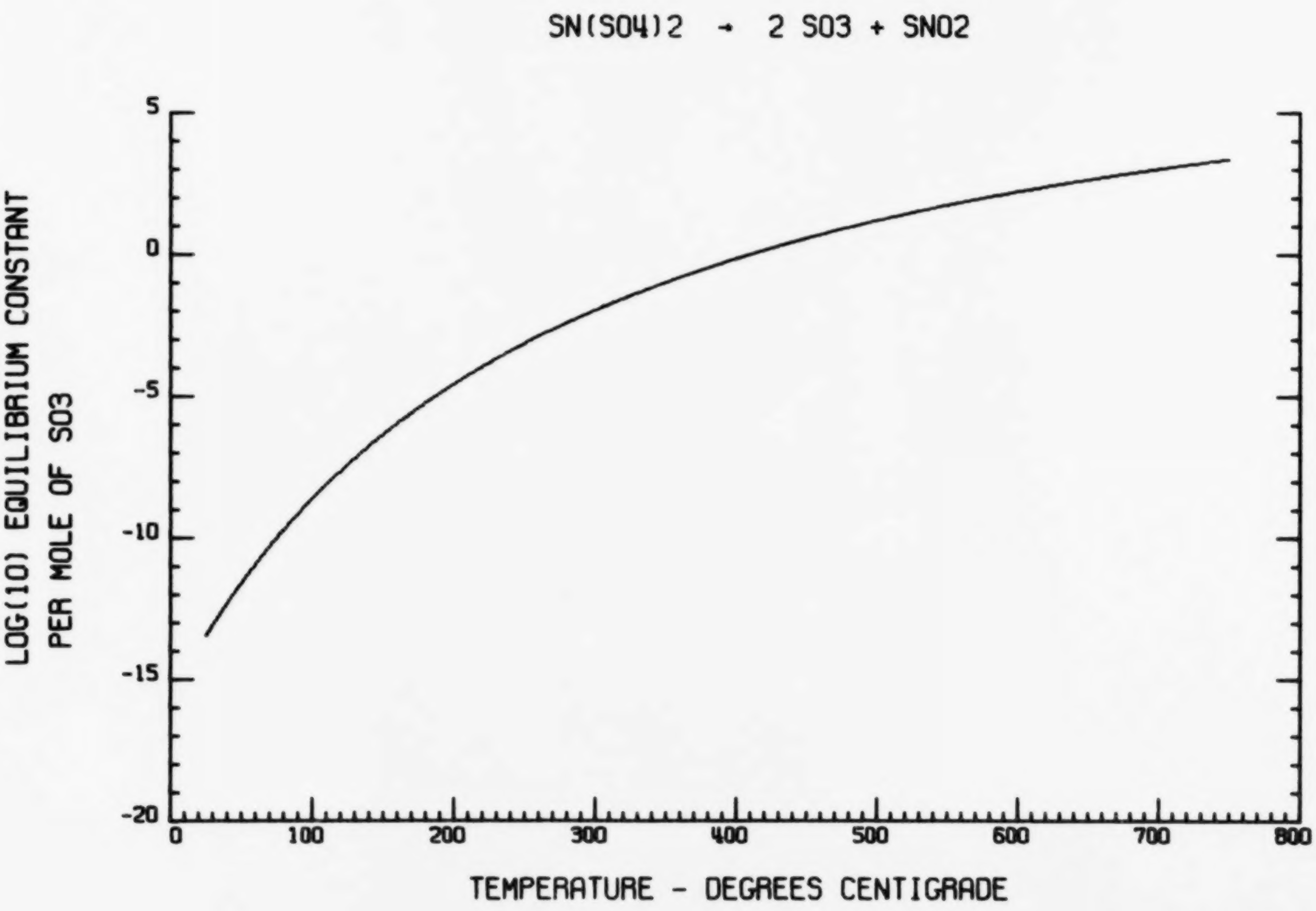
11 JUL 68

TRACOR

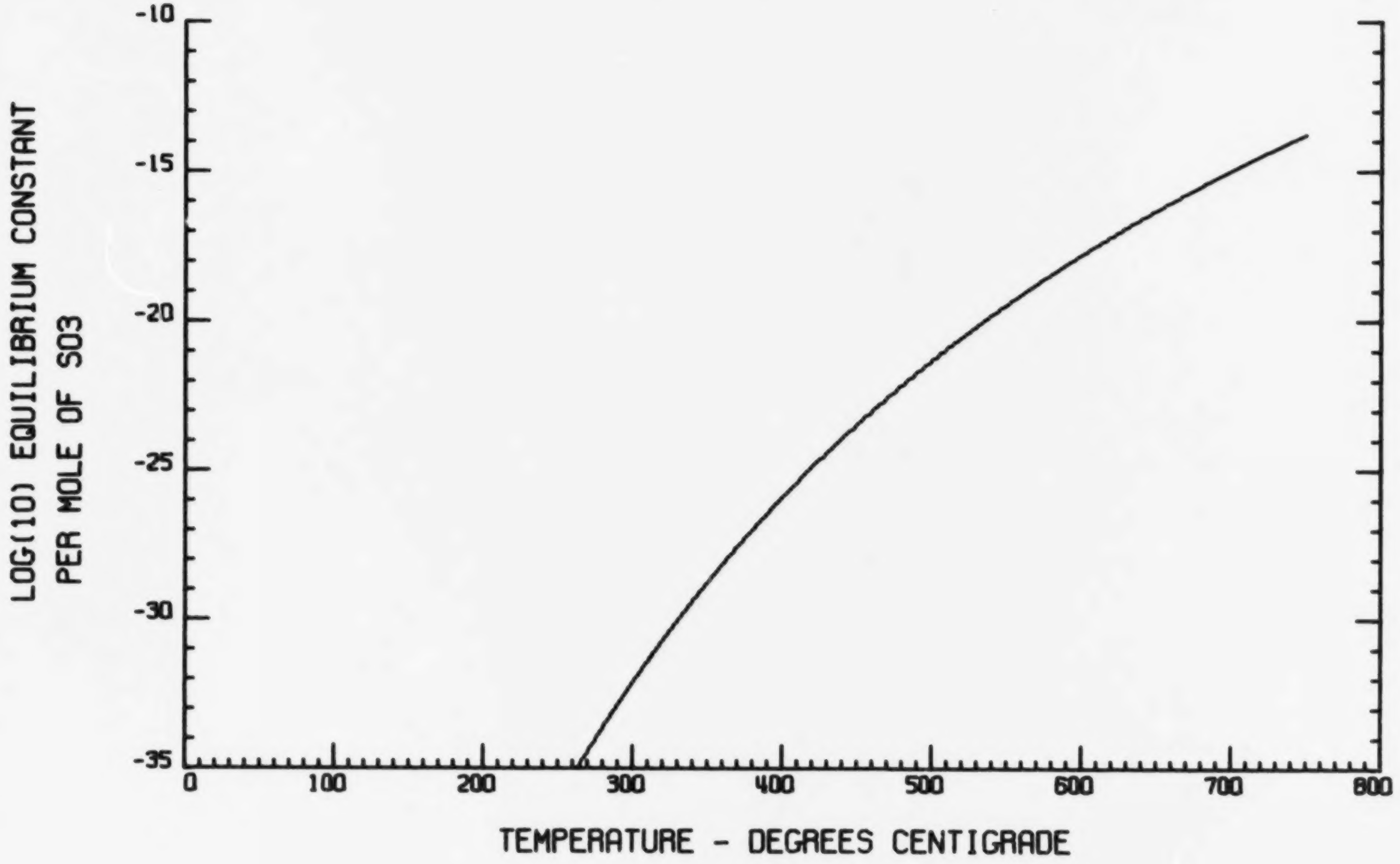

SB2(SO4)3 → 3 SO3 + SB2O3

21 OCT 68

TRACOR


SN(SO4)2 → 2 SO3 + SNO2
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO3
5
0
-5
-10
-15
-20
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

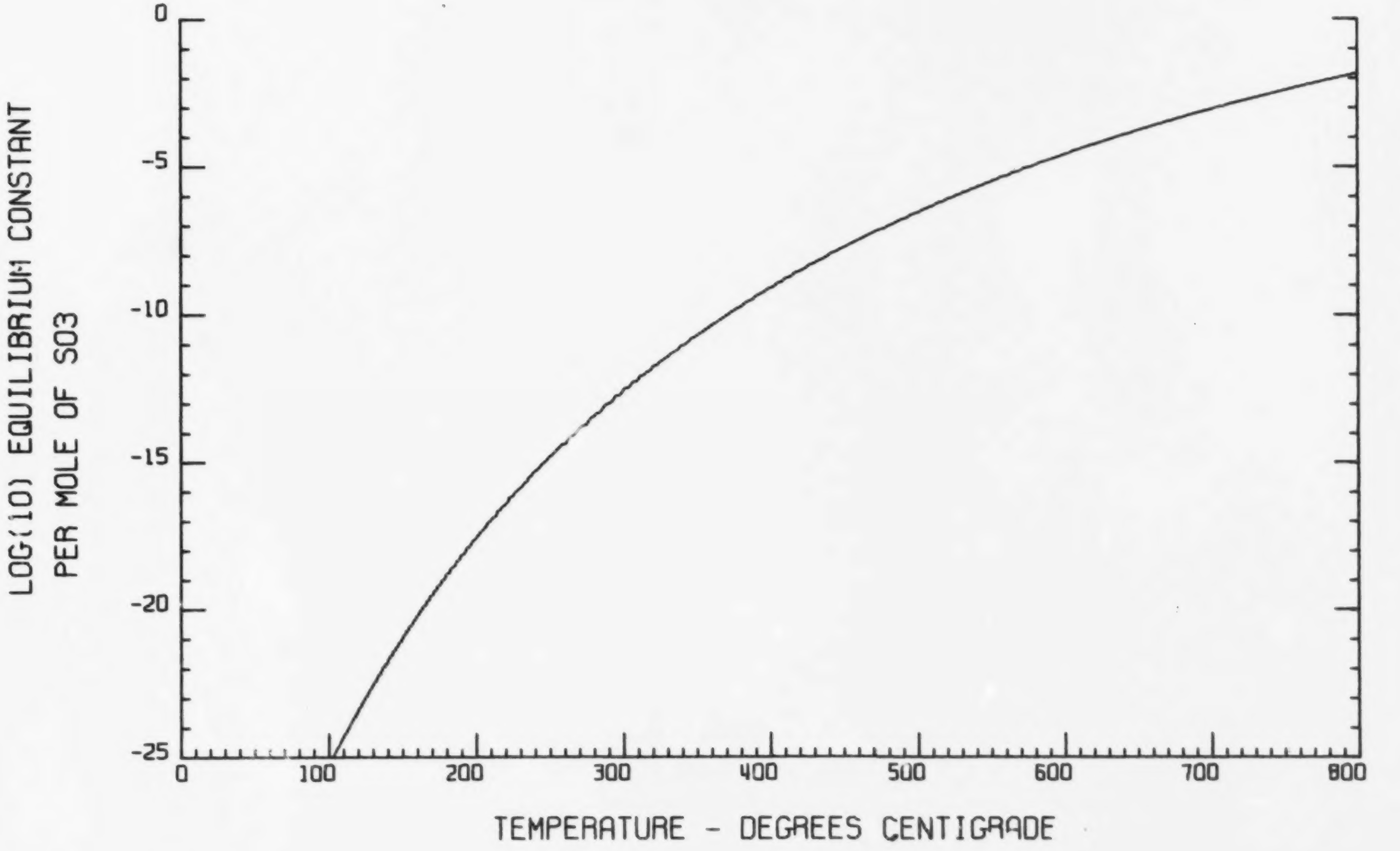
11 JUL 68



$SRSO_4 \rightarrow SO_3 + SRO$

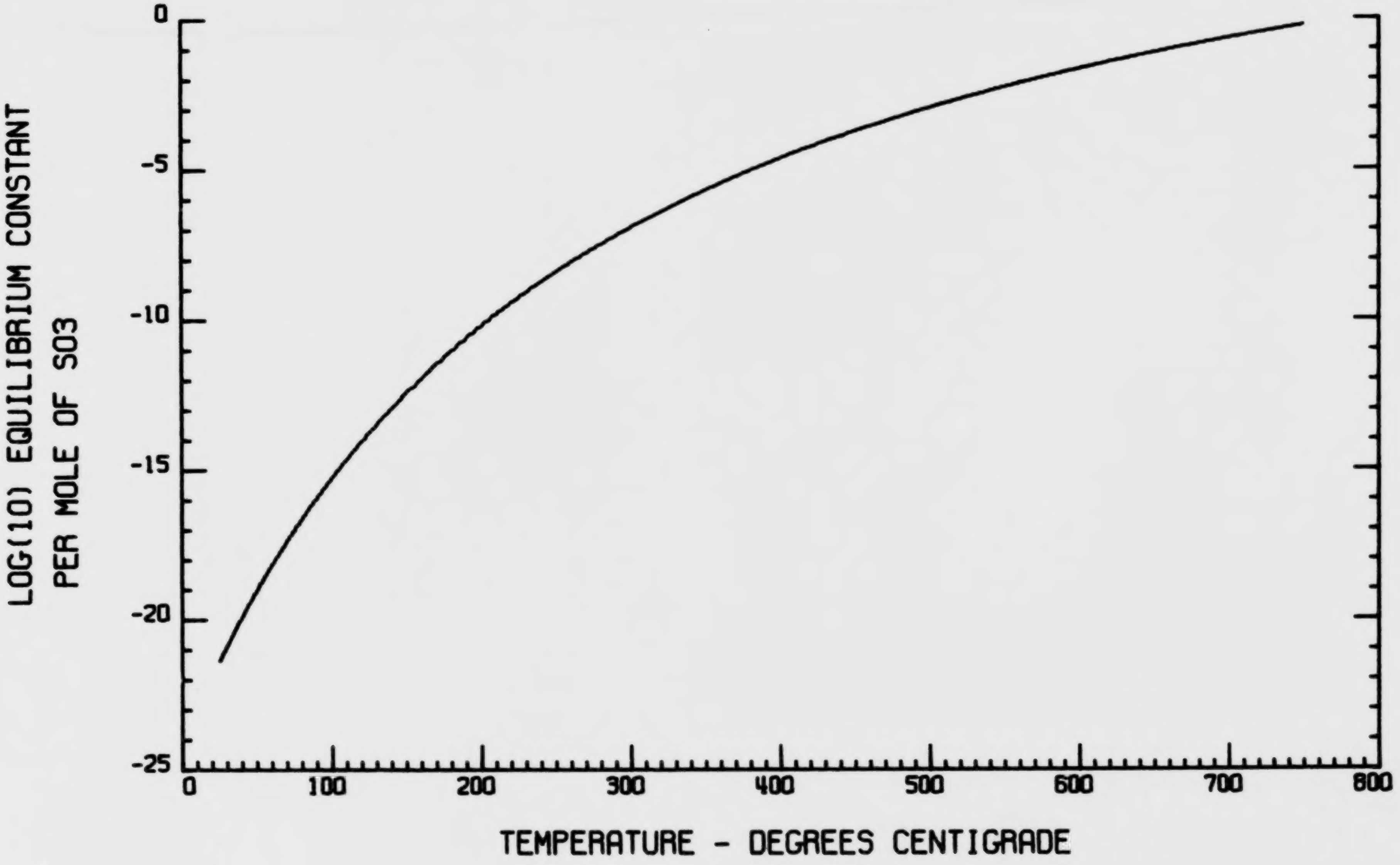
11 JUL 68

TH(SO4)2 → 2 SO3 + THO2

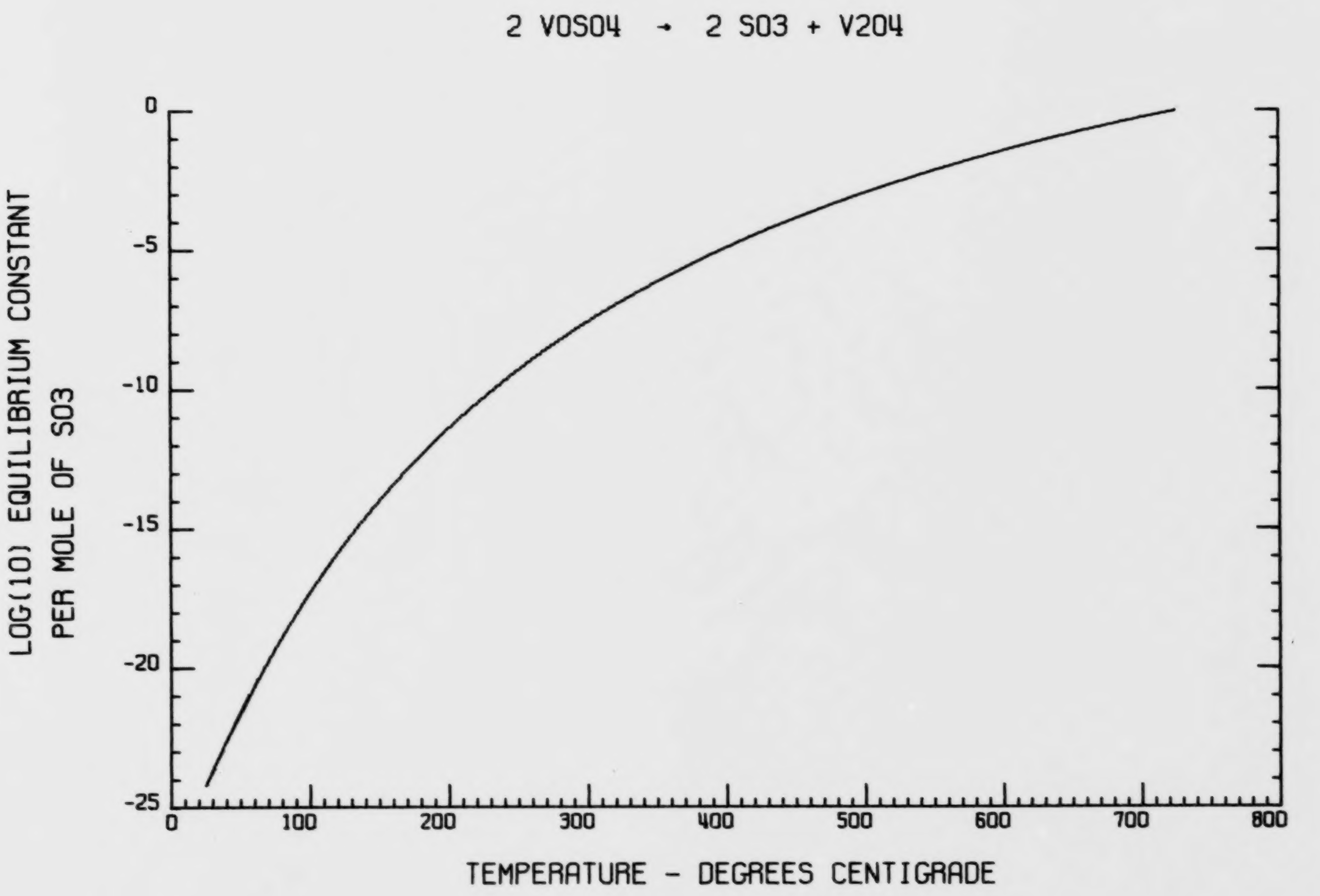


21 OCT 68

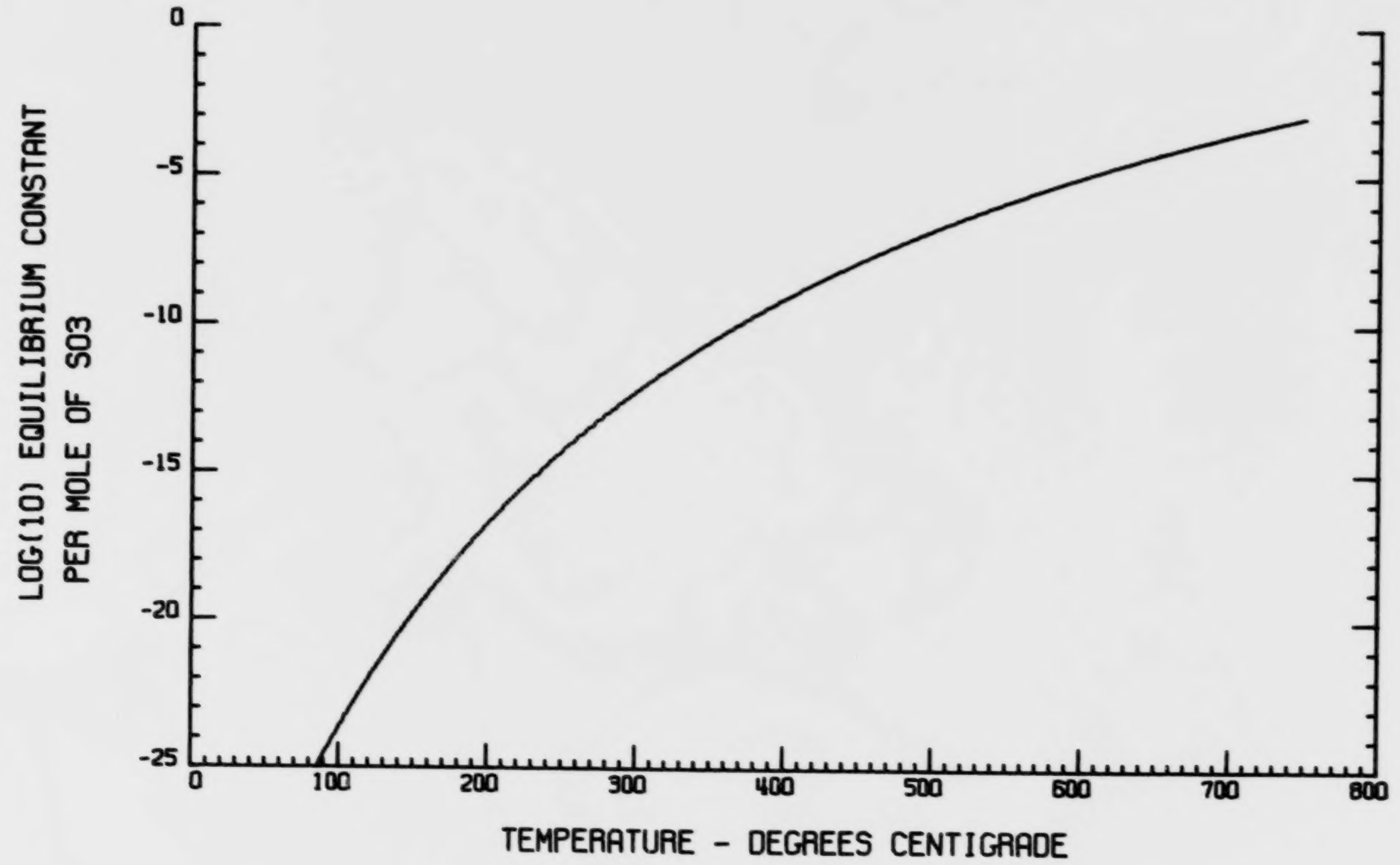
TRACOR


U(SO4)2 + 1/2 O2 → 2 SO3 + UO3

15 JUL 68

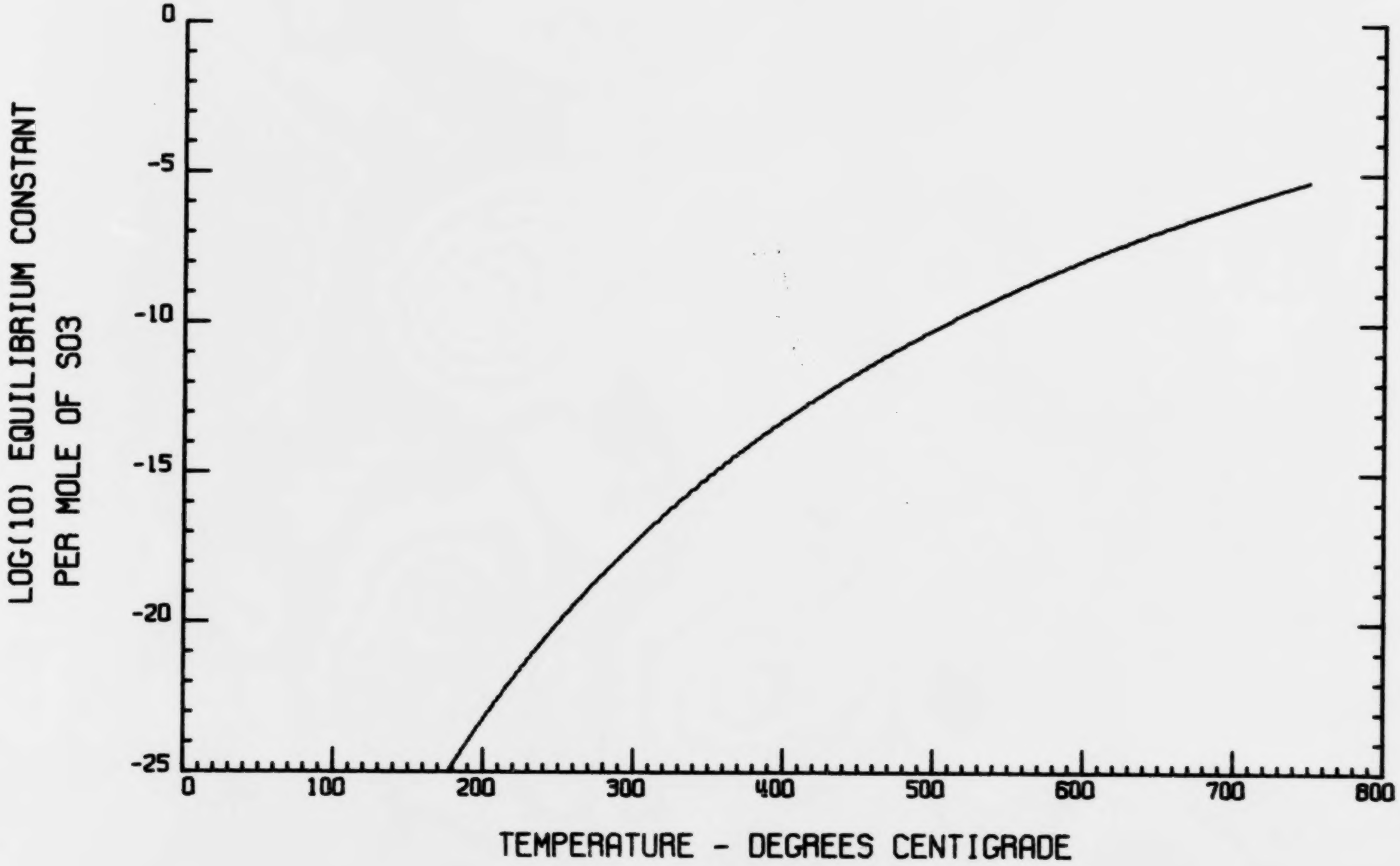

2 VOSO4 → 2 SO3 + V2O4
LOG(10) EQUILIBRIUM CONSTANT
PER MOLE OF SO3
0
-5
-10
-15
-20
-25
0
100
200
300
400
500
600
700
800
TEMPERATURE - DEGREES CENTIGRADE

09 AUG 68


ZNSO4 → SO3 + ZNO

11 JUL 68

ZR(SO4)2 → 2 SO3 + ZRO2



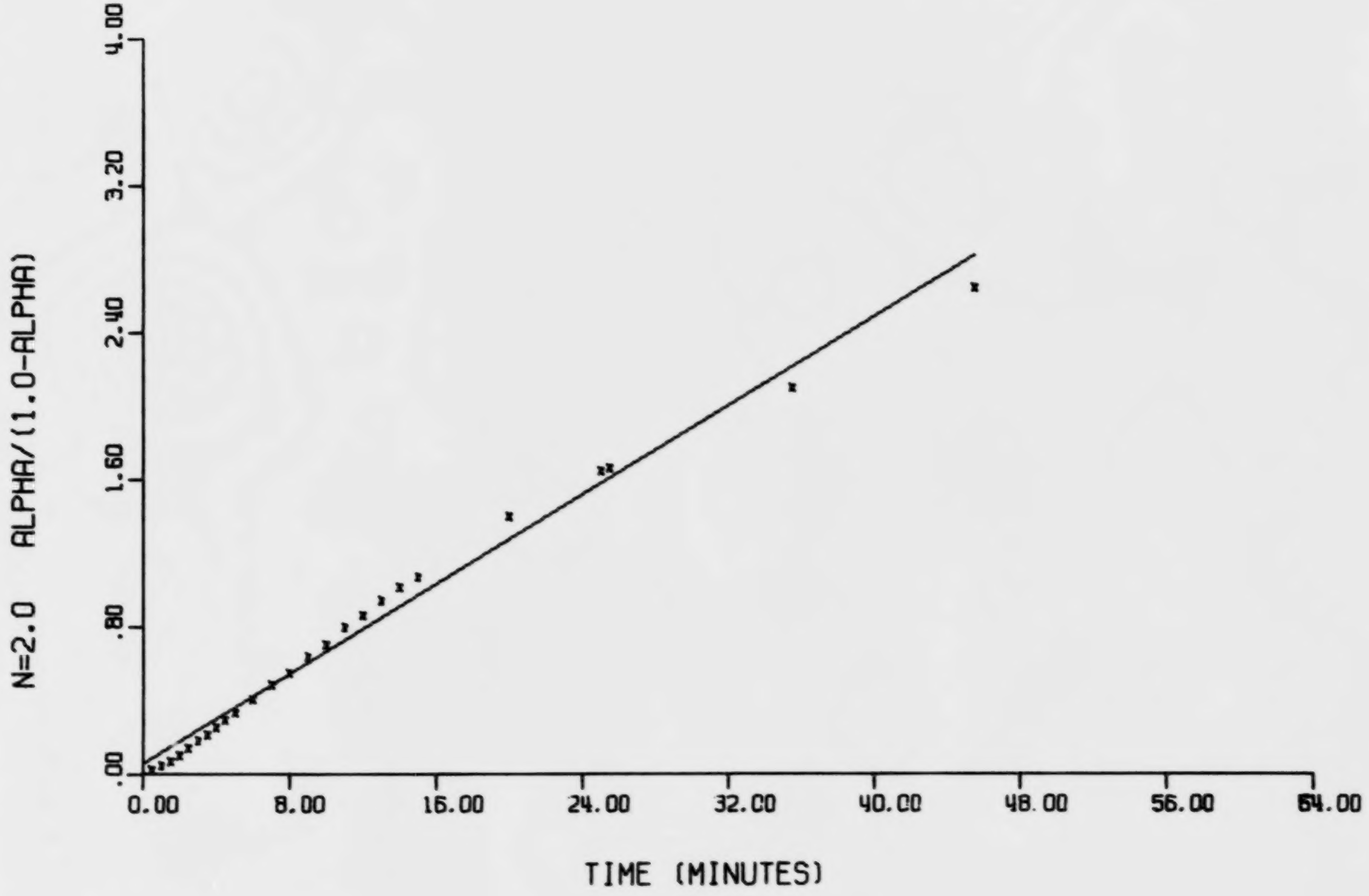
11 JUL 68

TRACOR

8.2 THERMODYNAMIC, KINETIC, AND ECONOMIC DATA

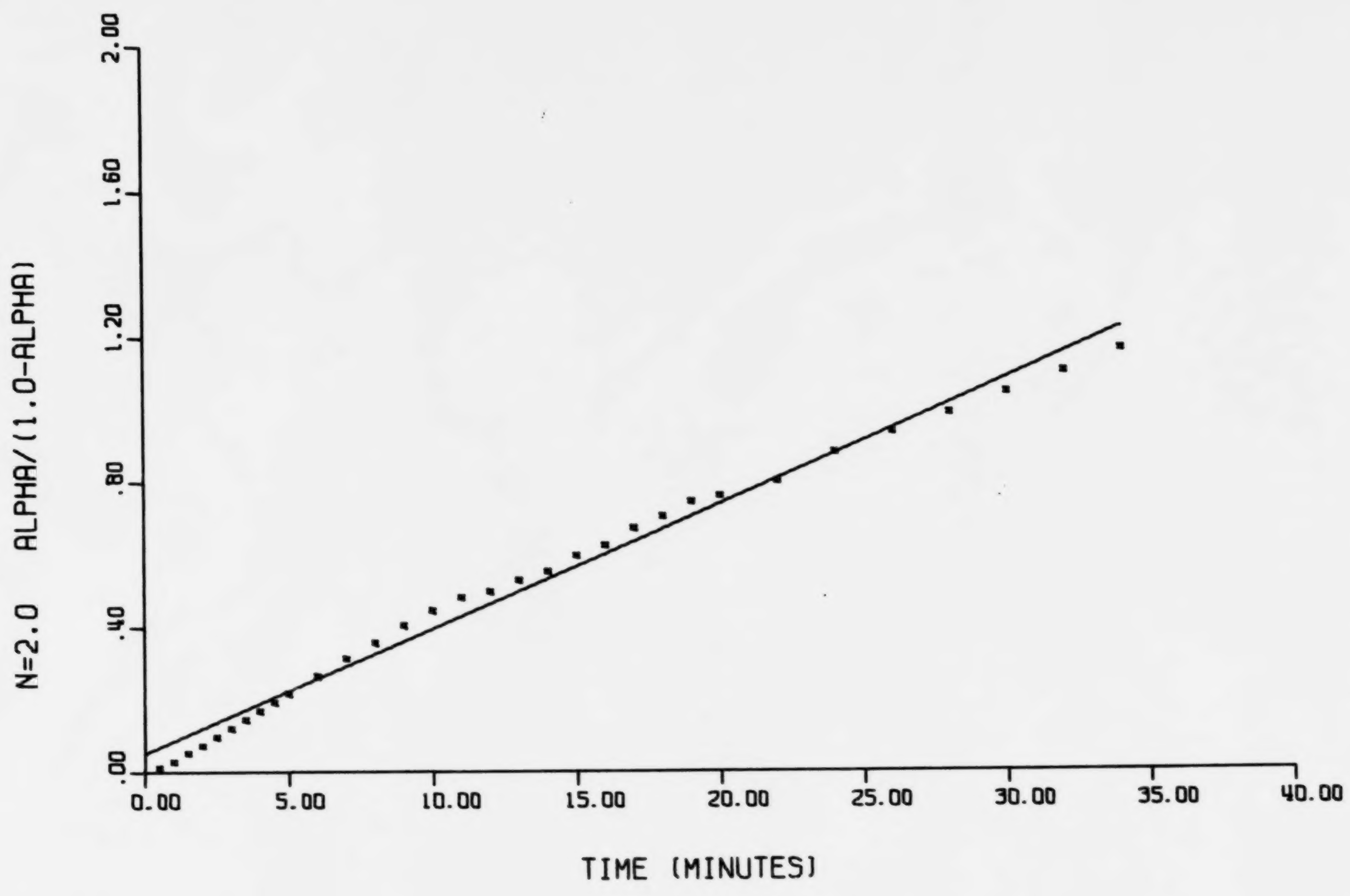
8.2.3 Plots of the Integrated Form of the Rate Equation

CE02 634-37-1
ISO TGA 3 TEMP = 191 DEG C



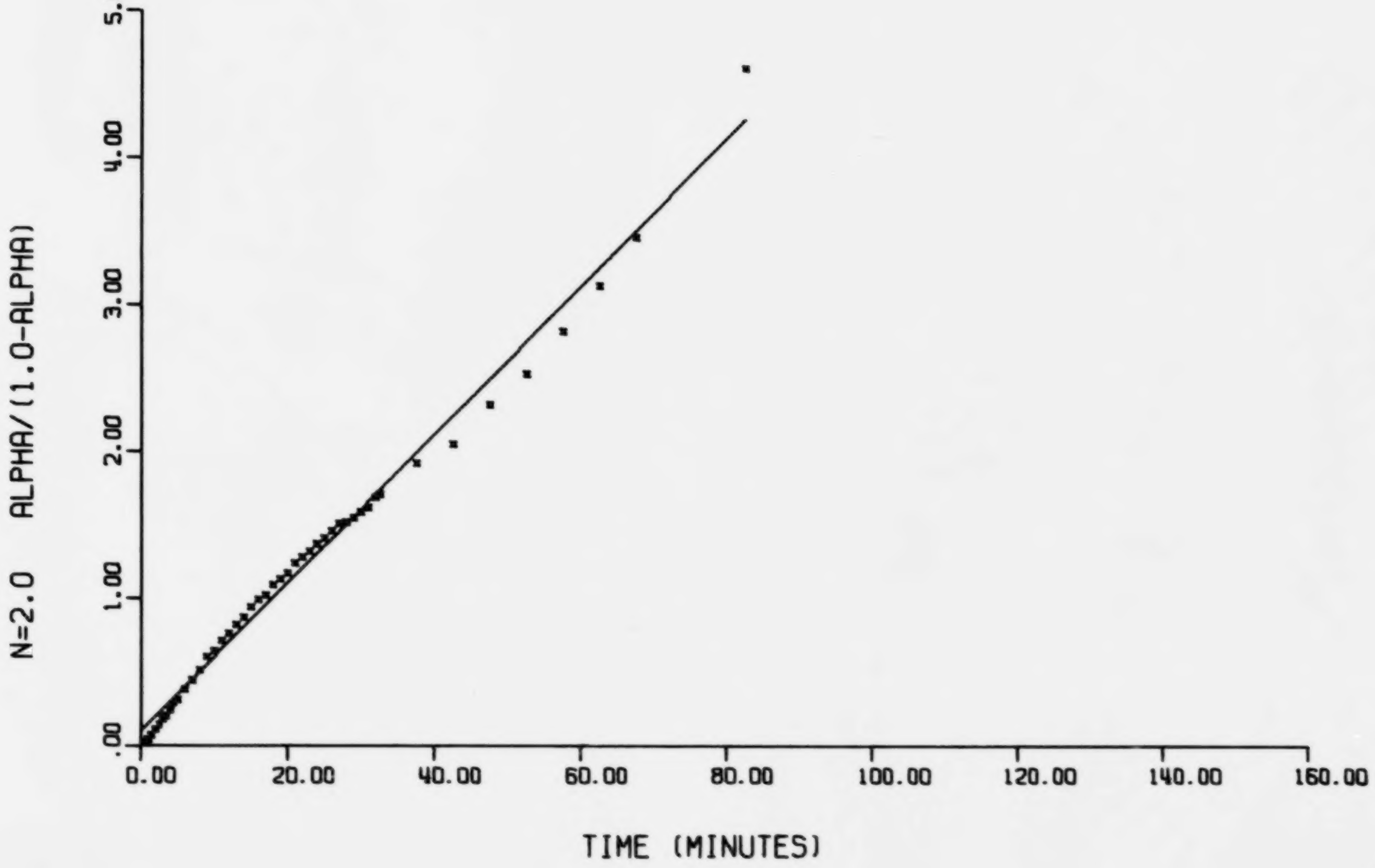
18 APR 69

CEO2 634-37-1
ISO TGA 5 TEMP = 238 DEG C



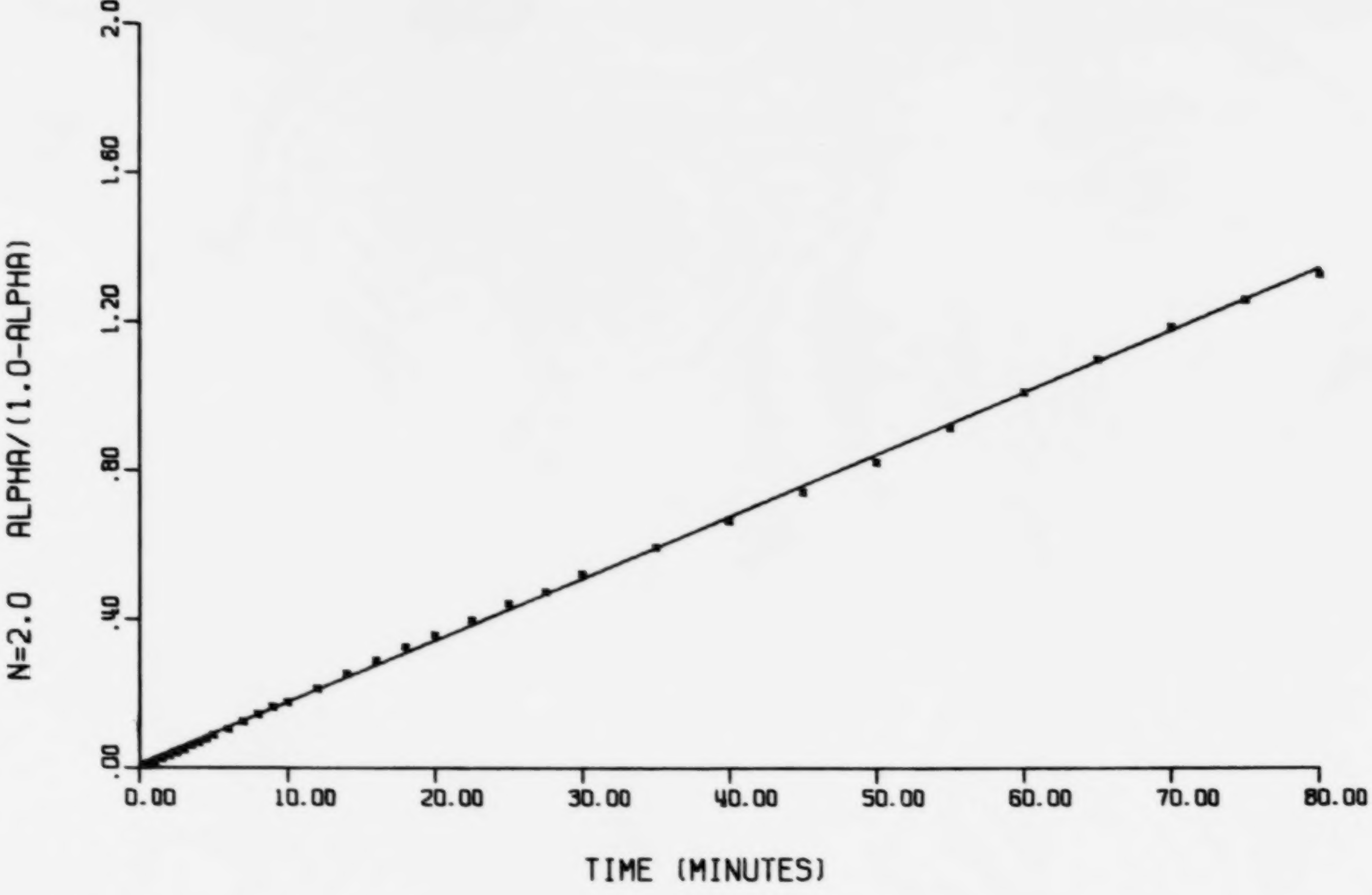
28 APR 69

CE02 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



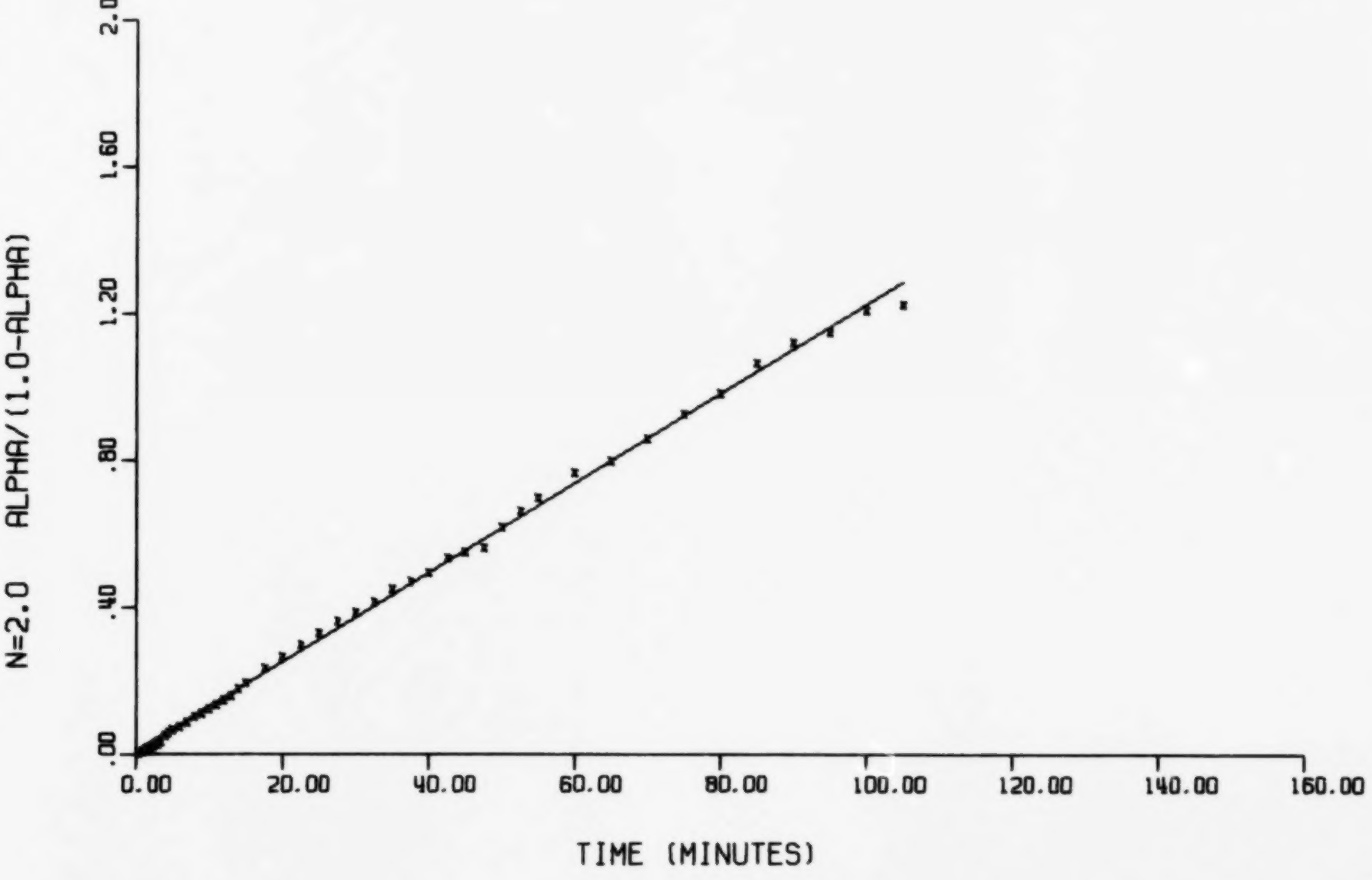
14 APR 69

CEO2 634-37-1
SO2 CONC = 0.190 TEMP = 196 DEG C



3 JUN 69

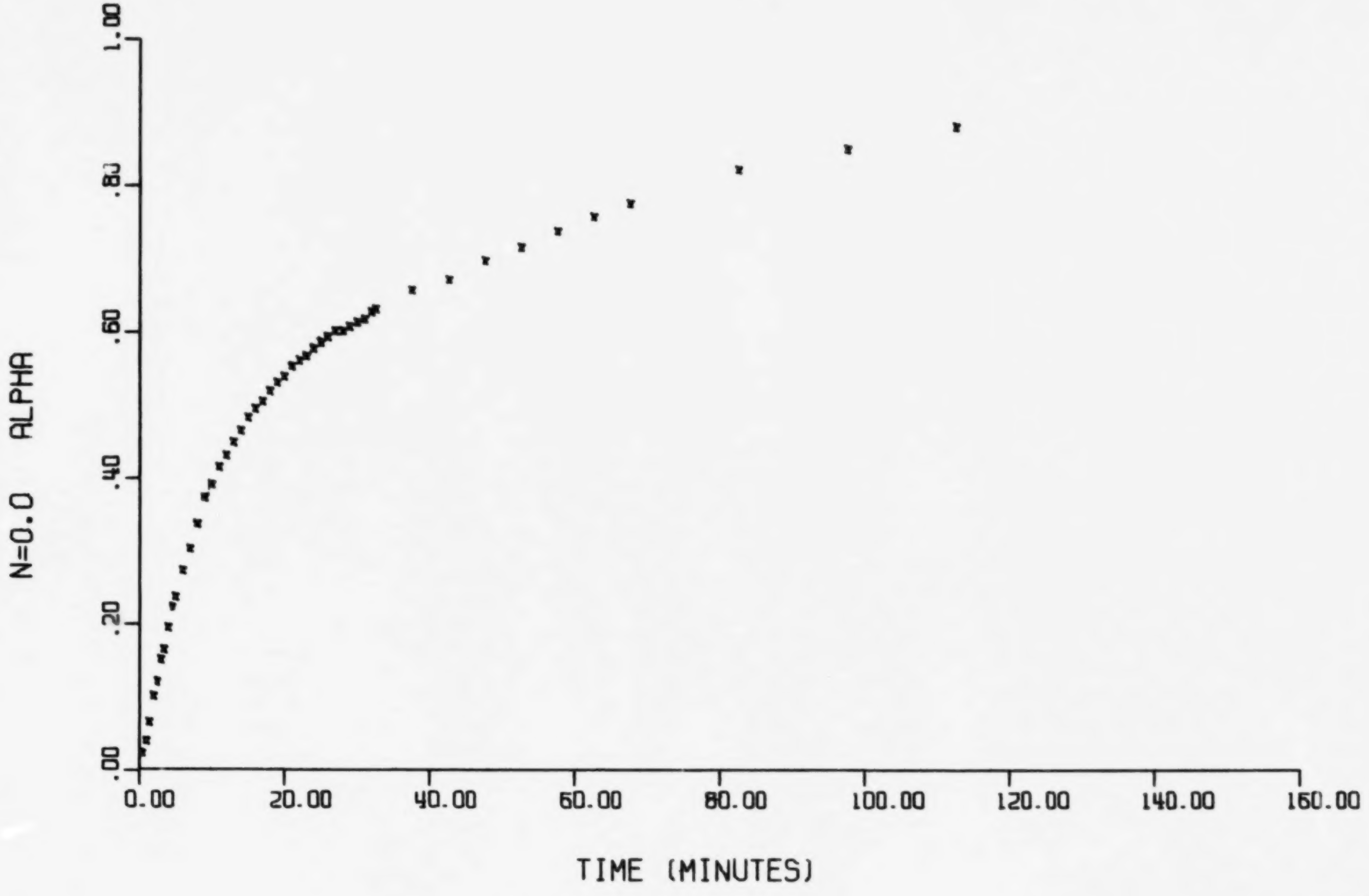
CEO2 634-37-1
SO2 CONC 0.127 TEMP = 194 DEG C



18 APR 69

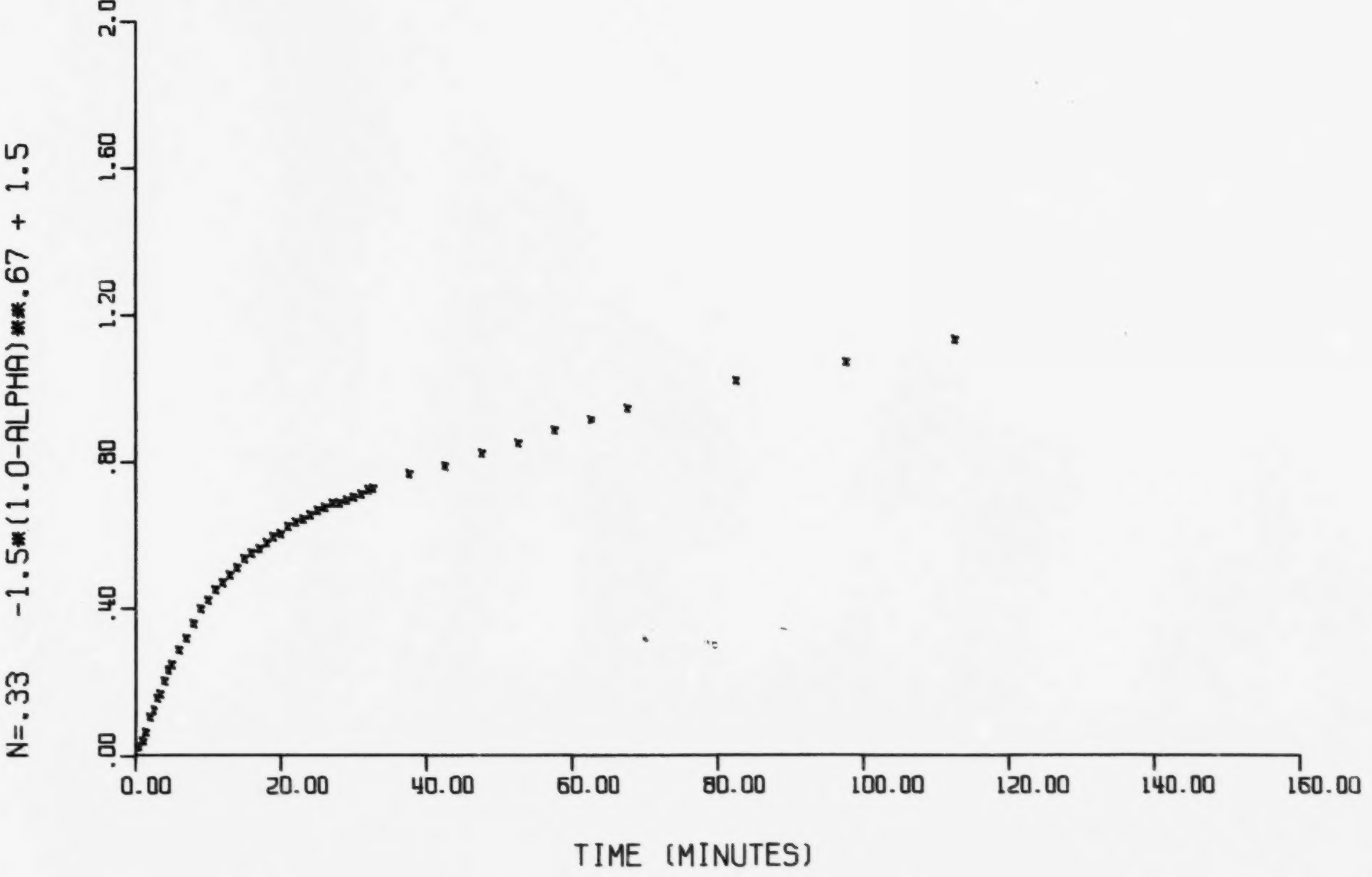
TRACOR

CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

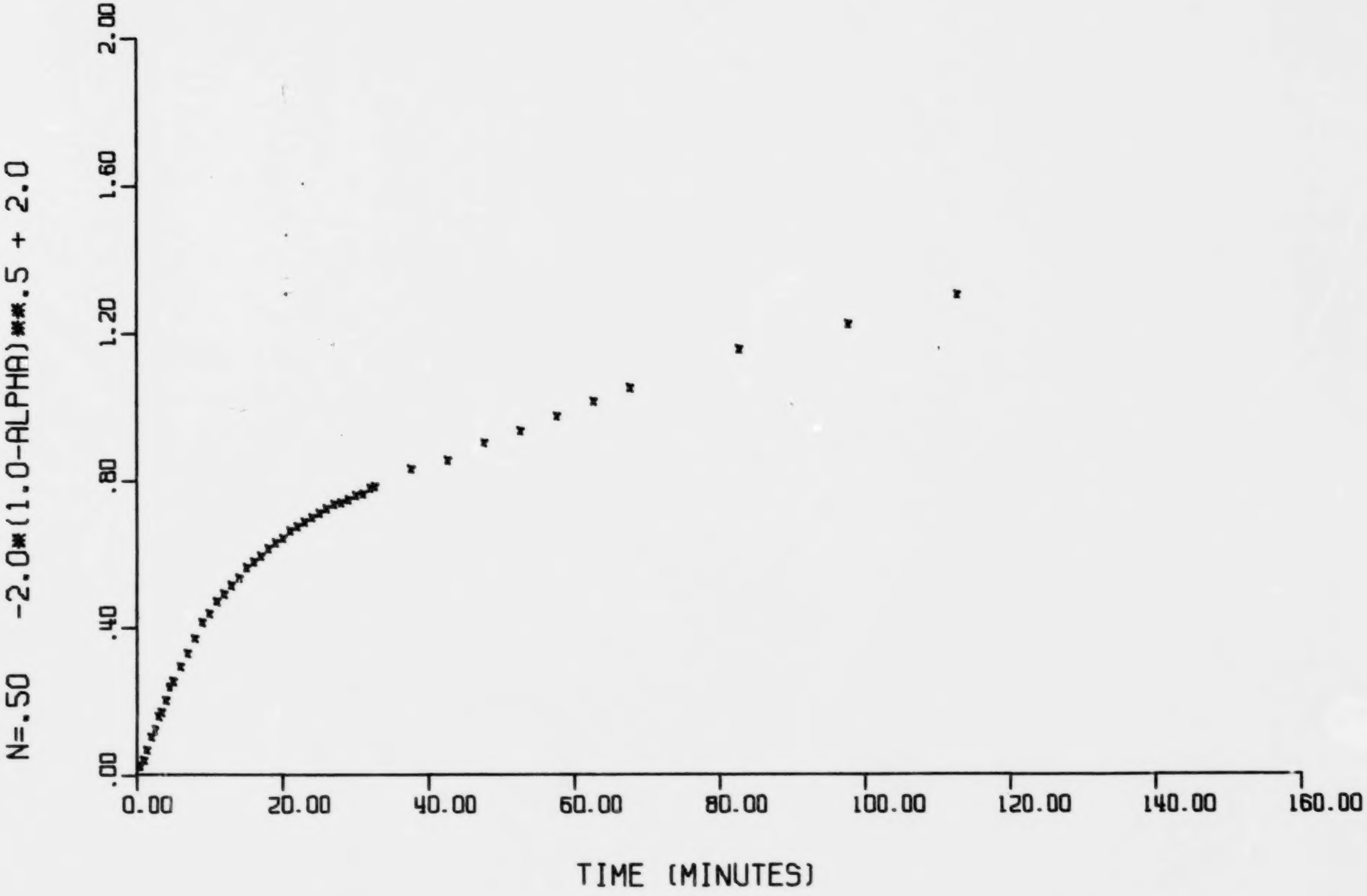
CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

TRĀCOR

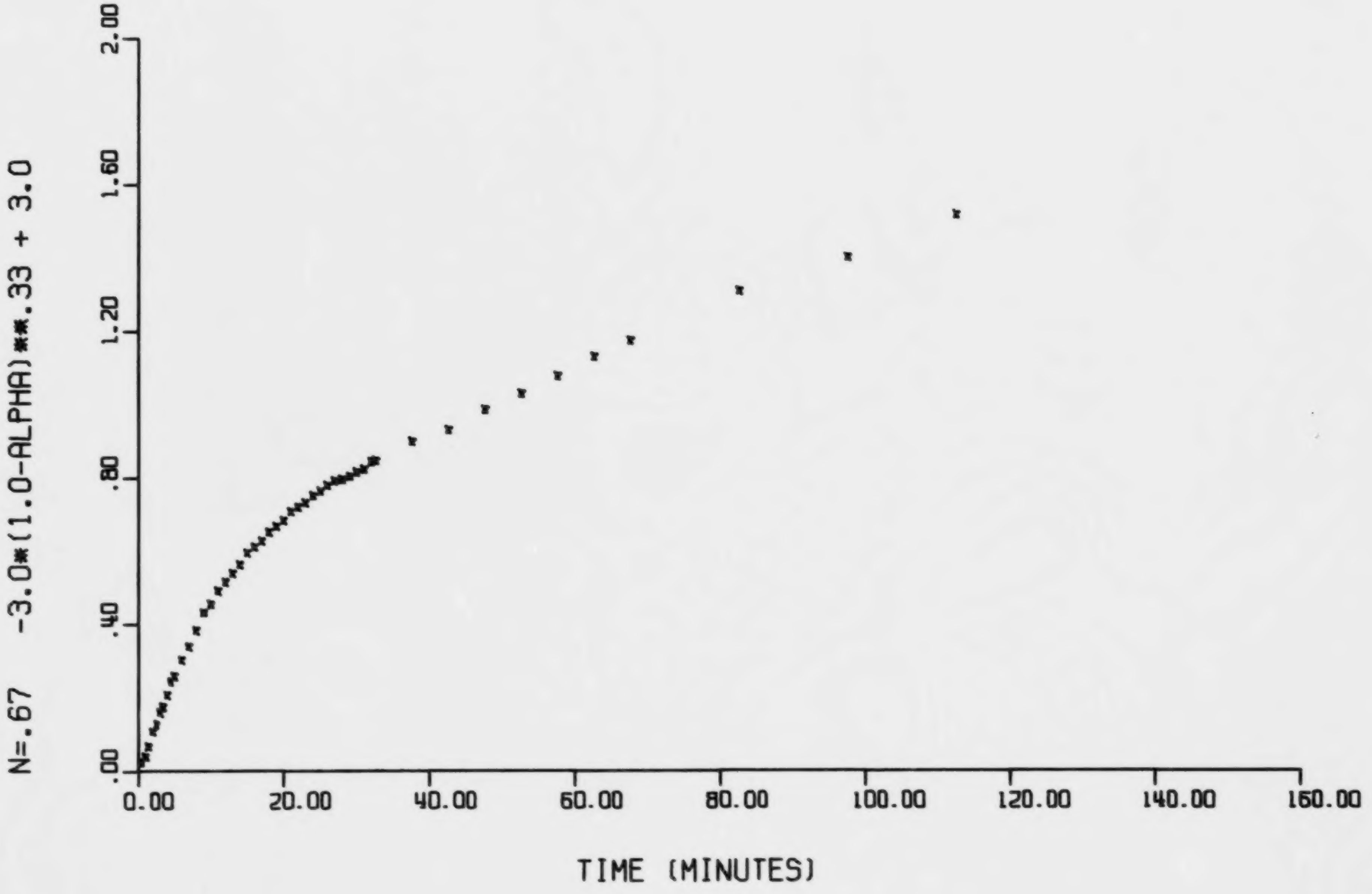
CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

TRACOR

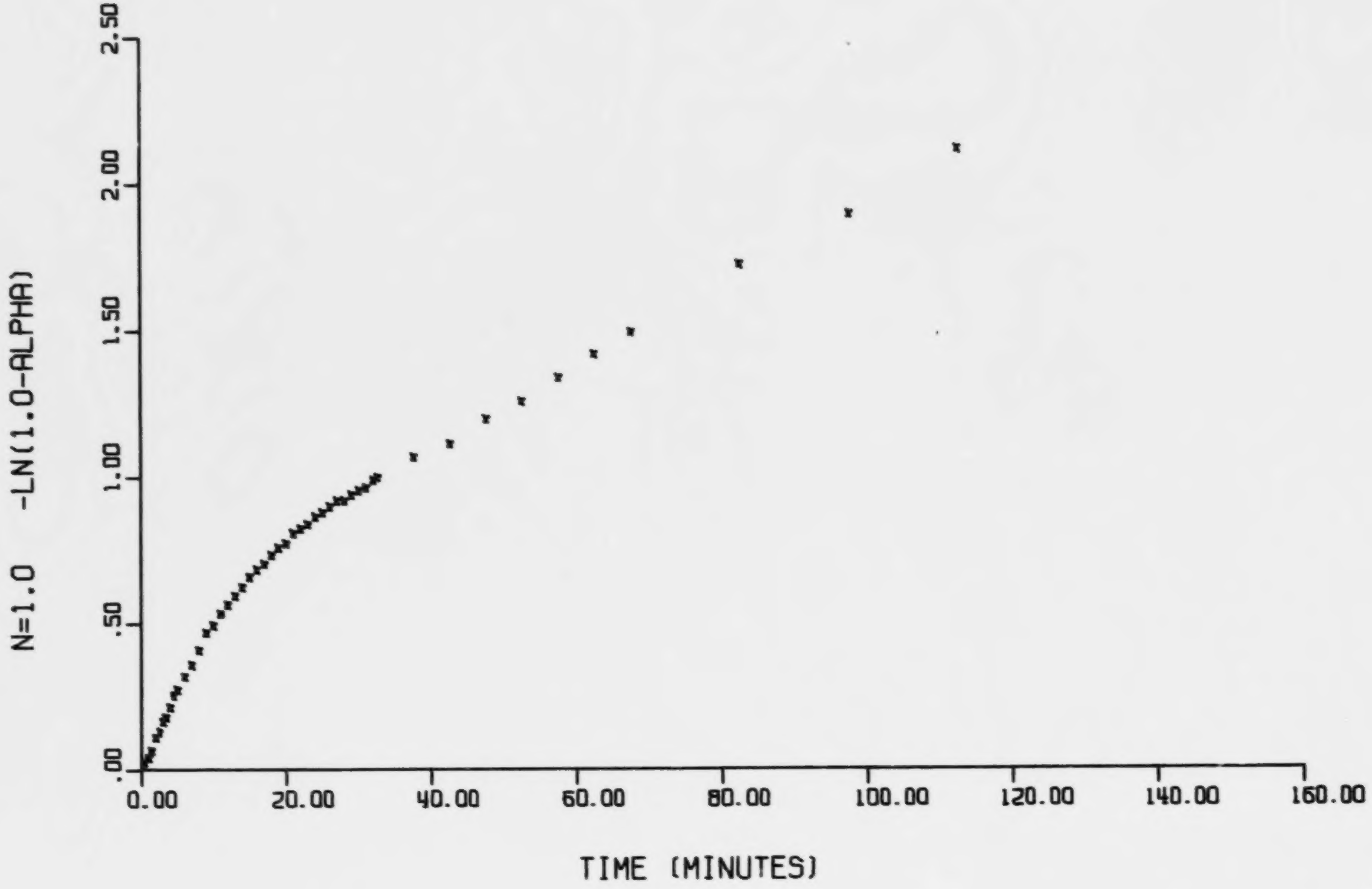
CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

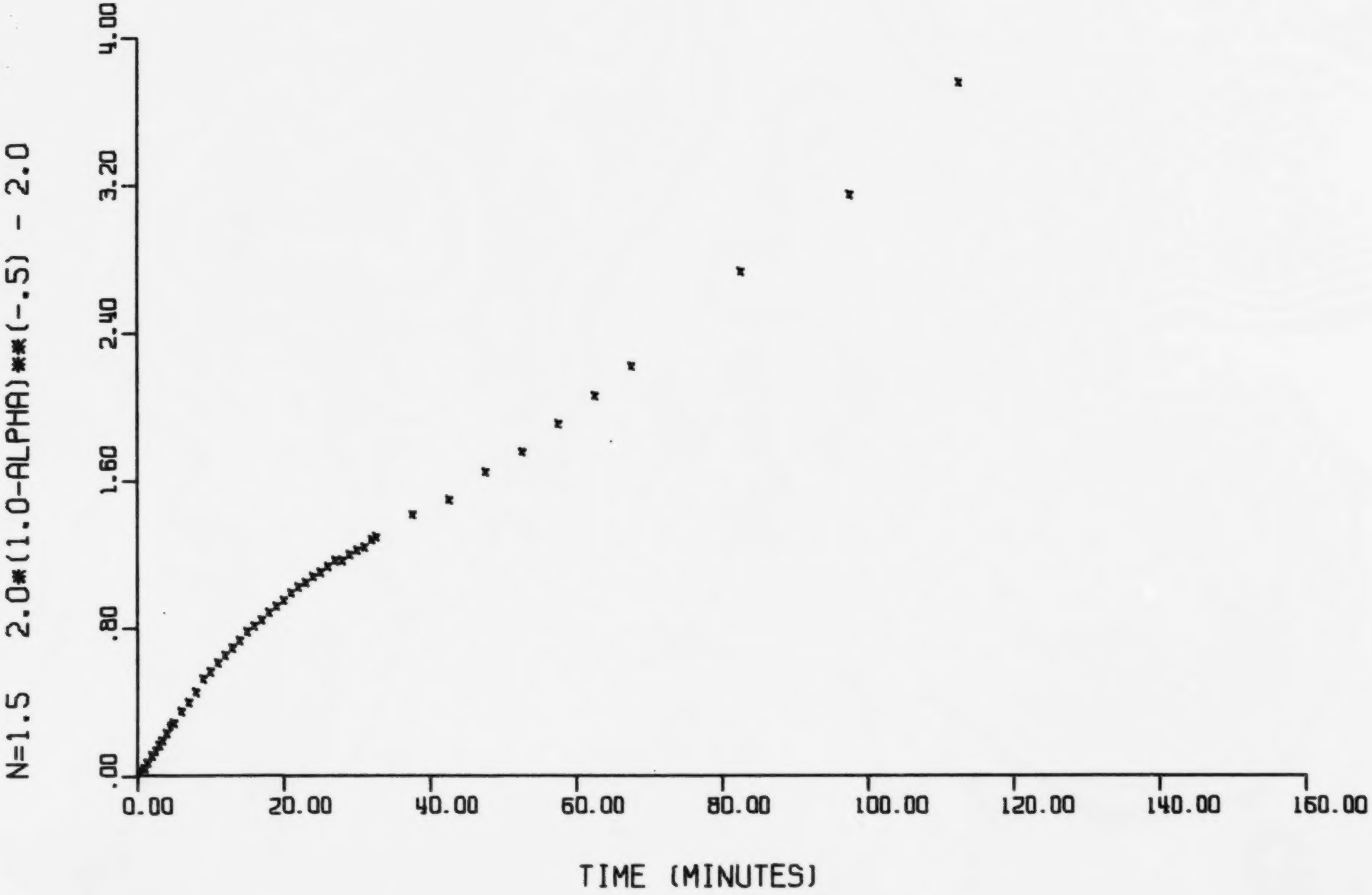
TRACOR

CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.

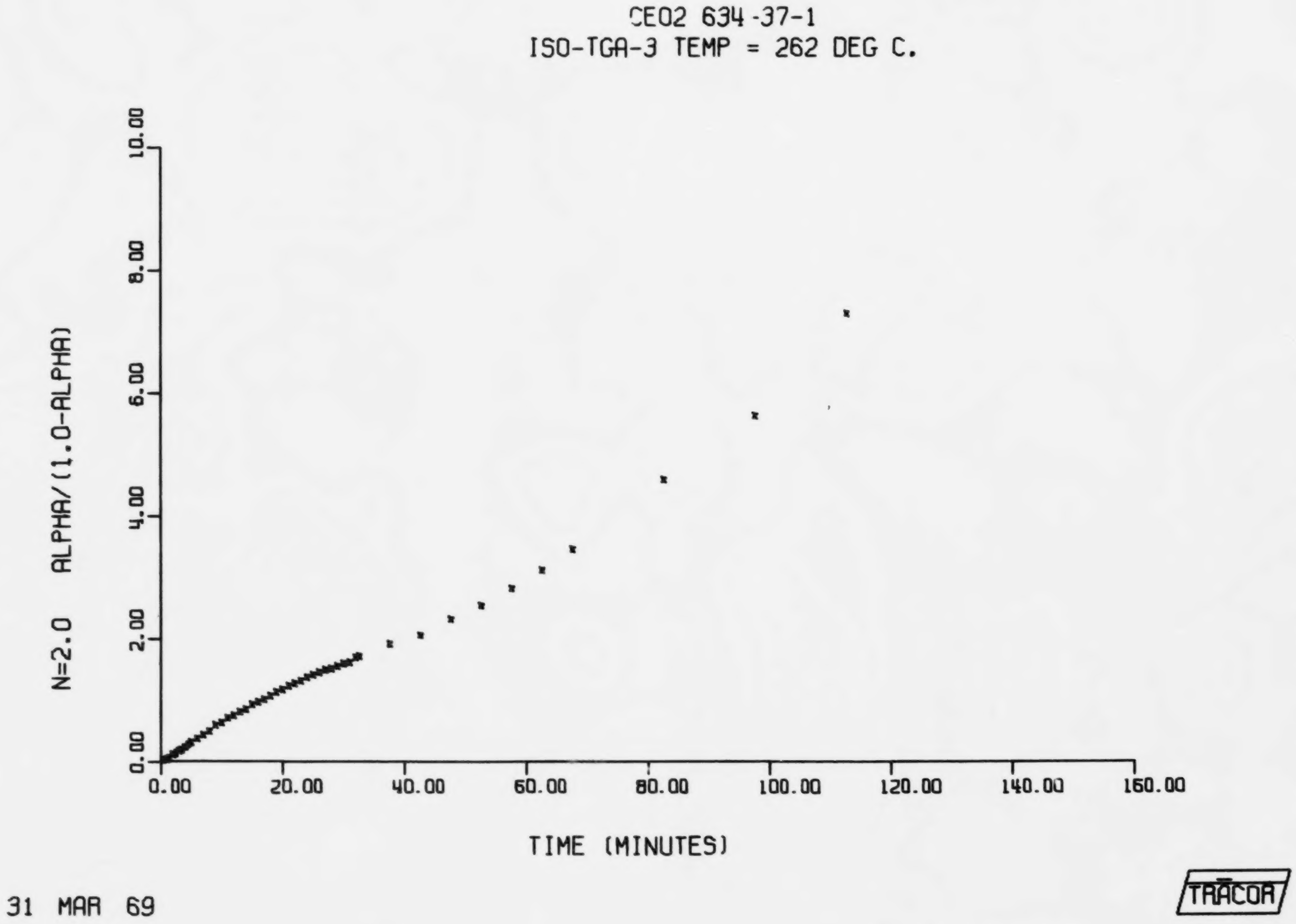


31 MAR 69

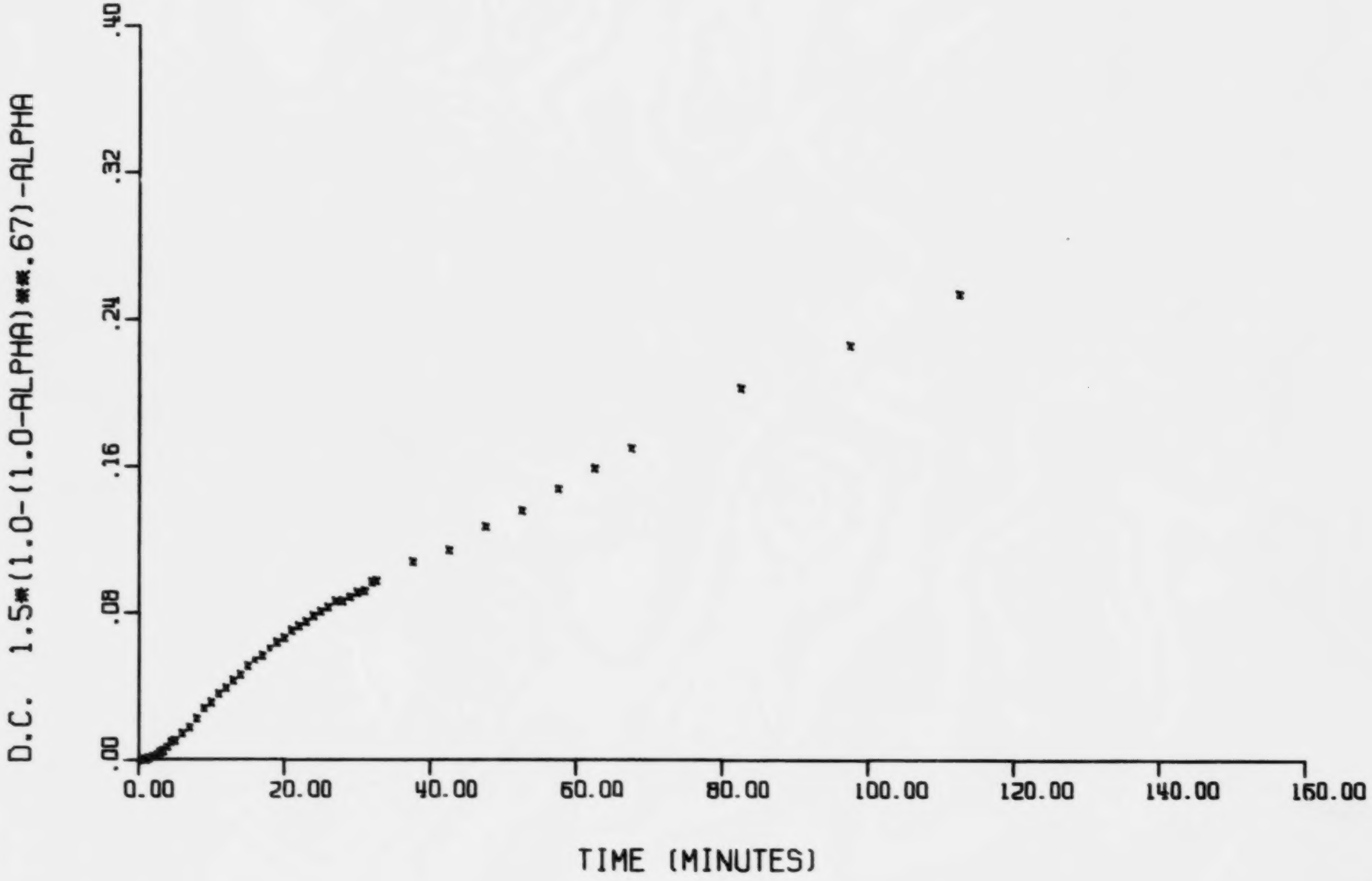
CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

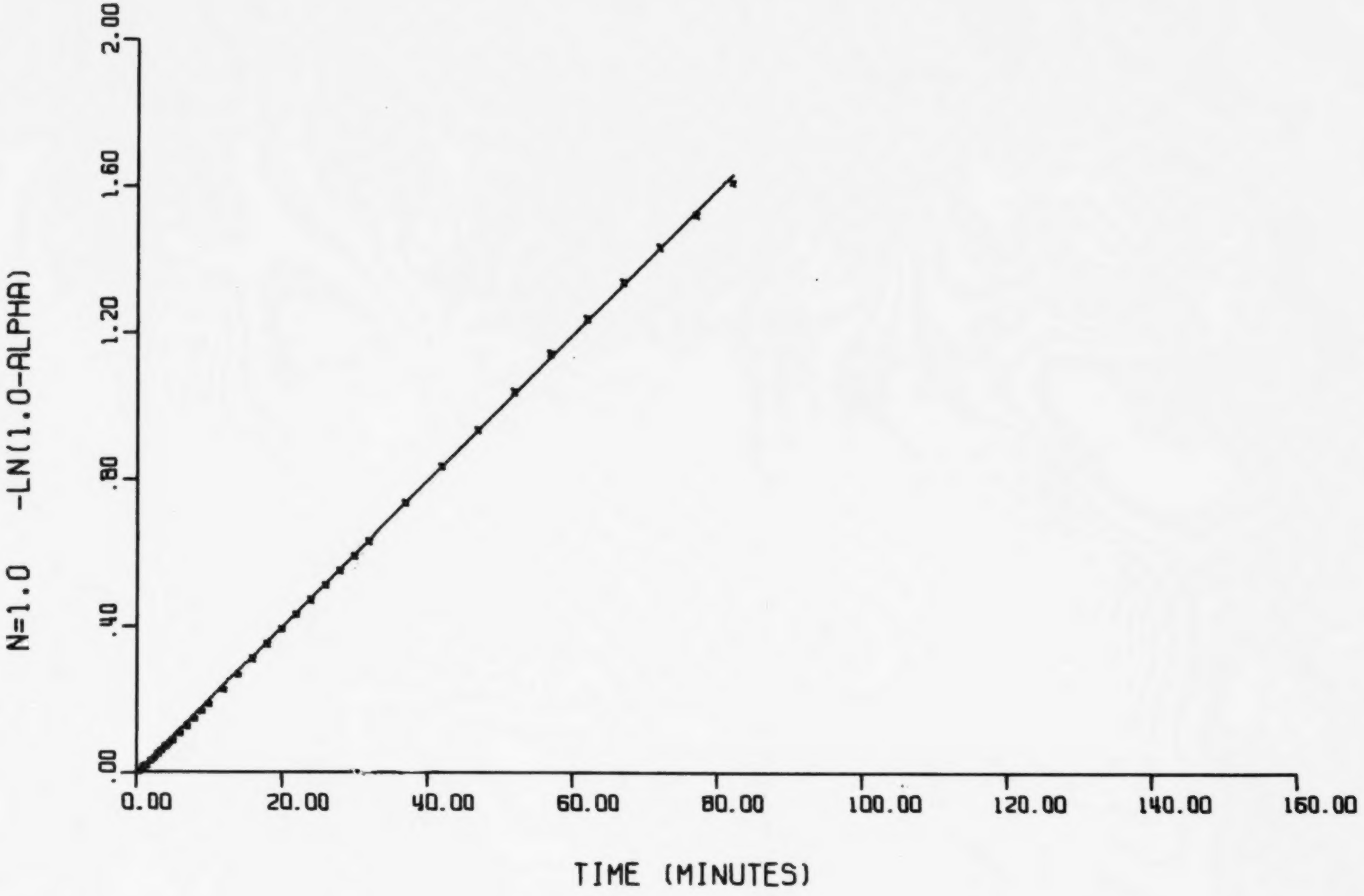

CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.
N=2.0 ALPHA/(1.0-ALPHA)
0.00
2.00
4.00
6.00
8.00
10.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
TIME (MINUTES)
31 MAR 69
TRACOR

CEO2 634-37-1
ISO-TGA-3 TEMP = 262 DEG C.



31 MAR 69

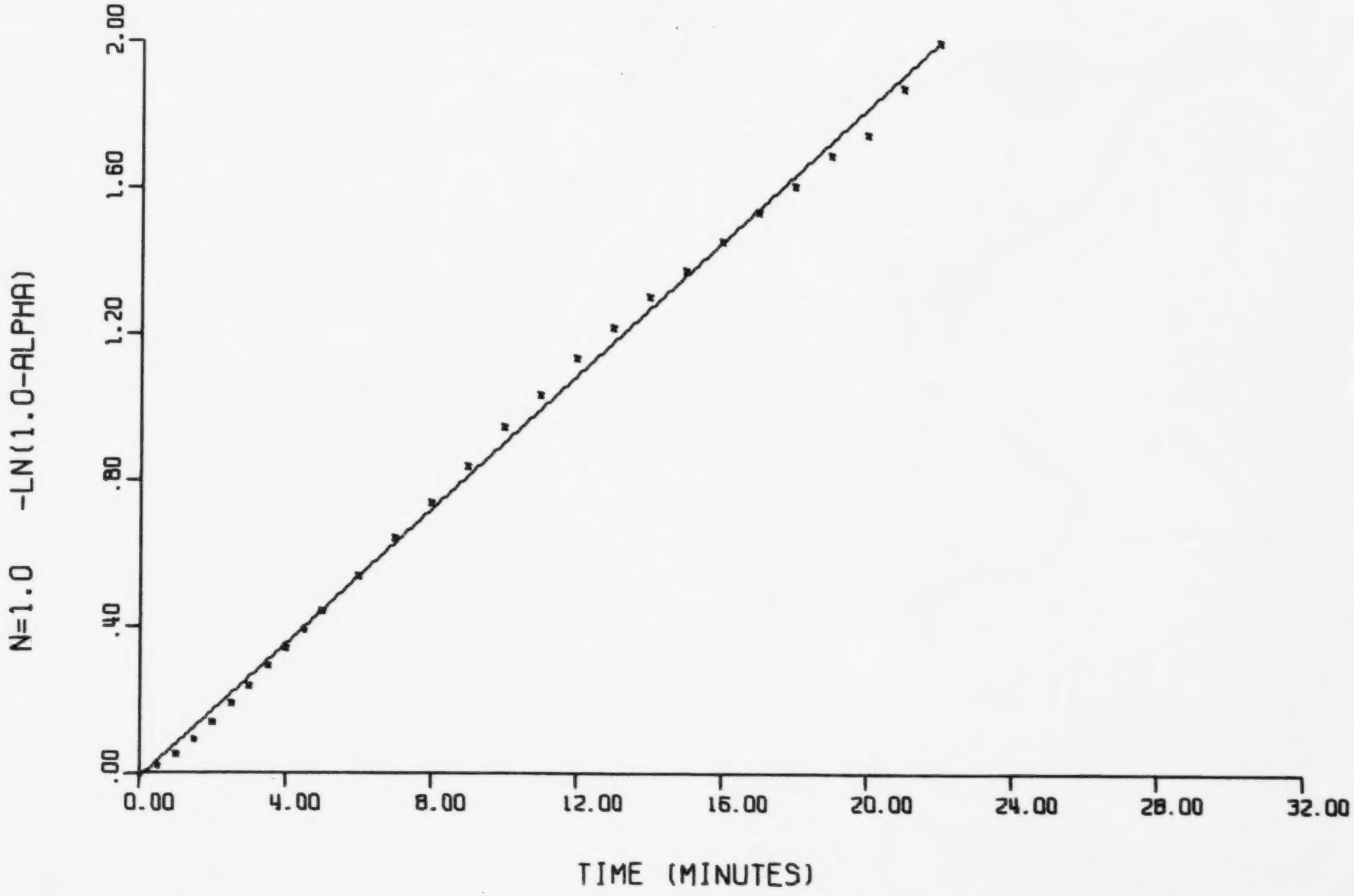
TRACOR



CO3O4 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.
w_o/m_o=0.38

2 APR 69

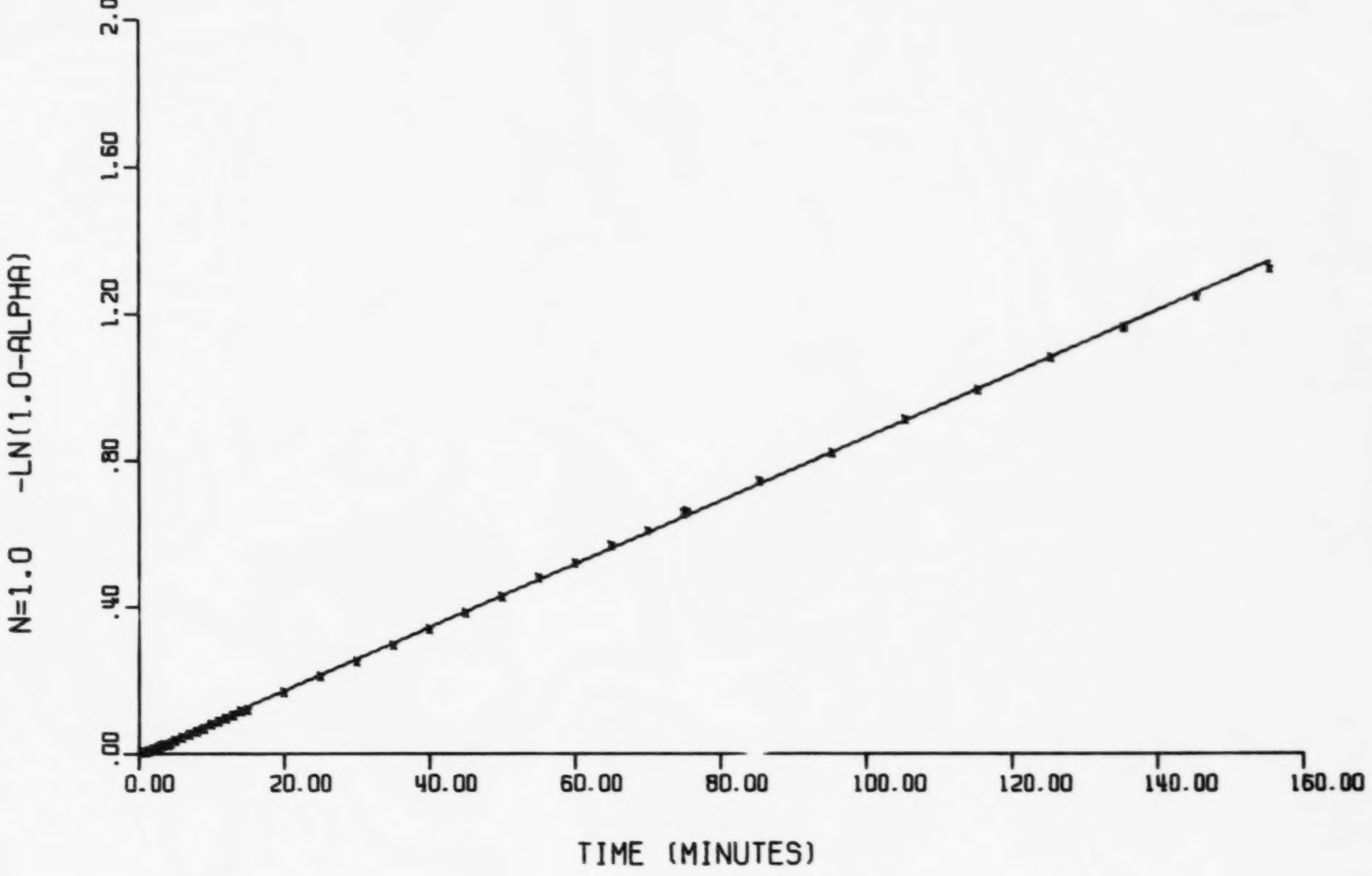
CO3O4 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
$w_o/m_o = 0.38$



2 APR 69

TRACOR

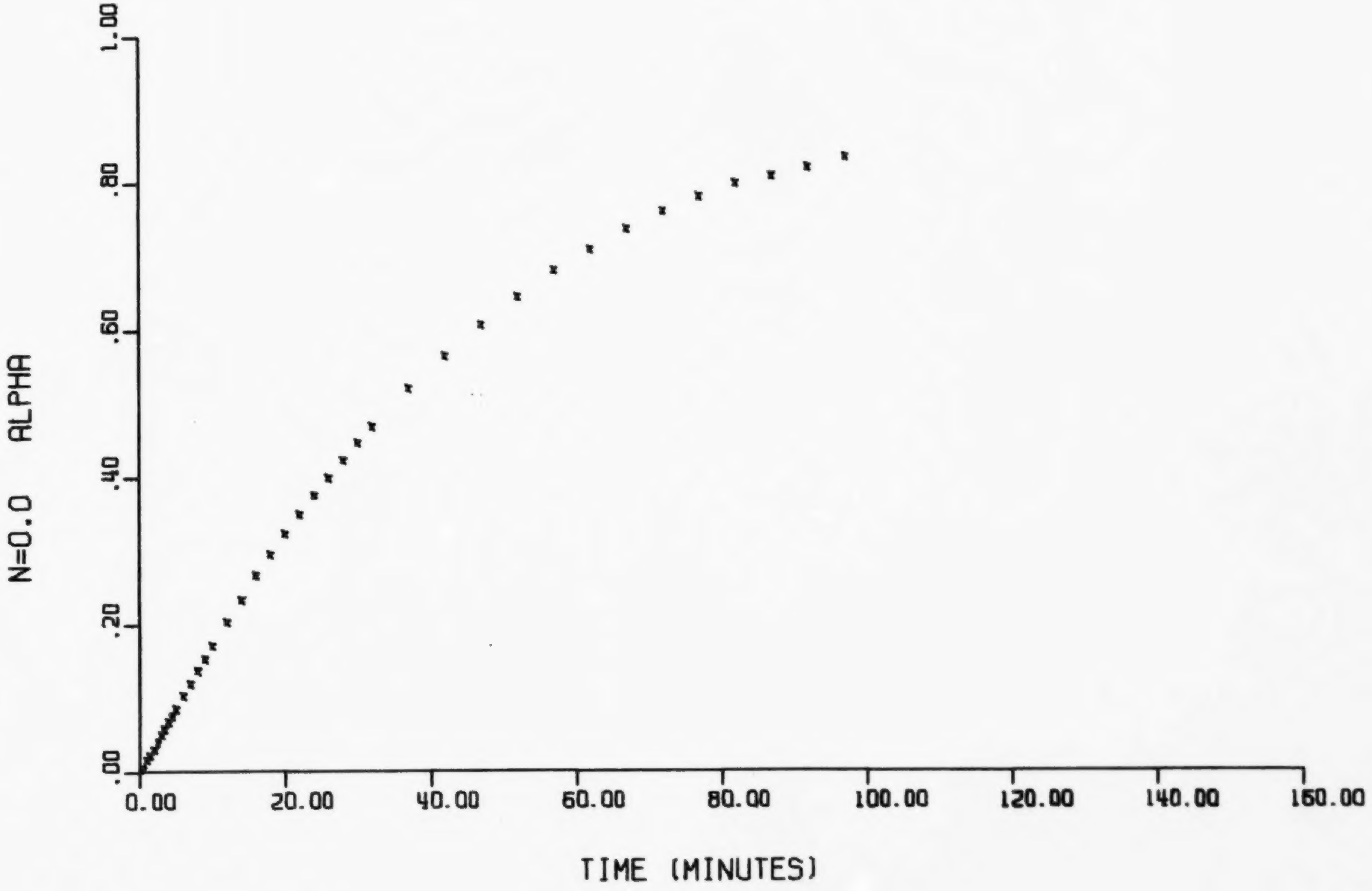
CO304 634-43-1
SO2 CONC = 0.129 TEMP = 453 DEG C
$w_o/m_o=0.38$



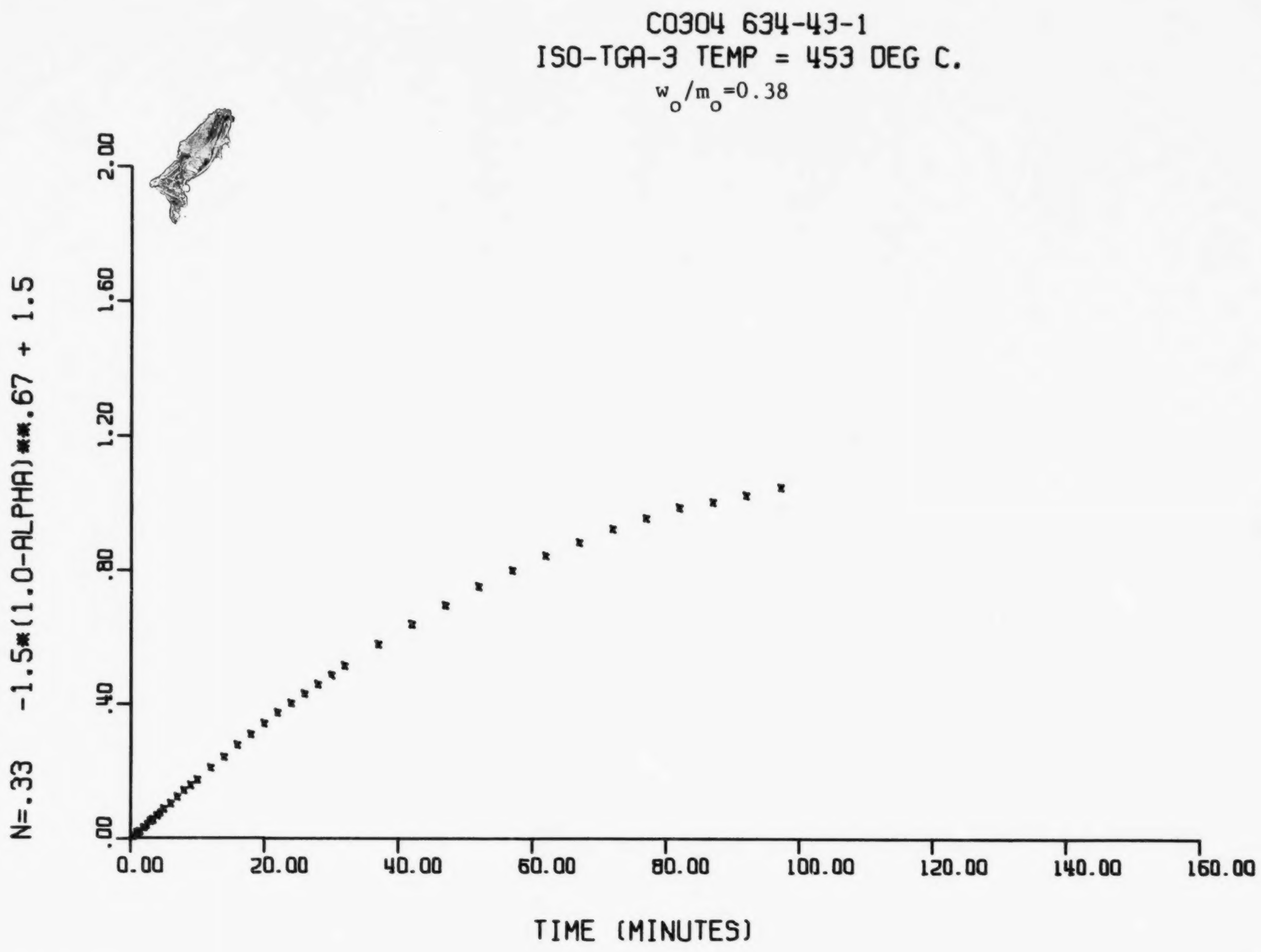
15 APR 69

CO304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.

w_o/m_o=0.38



31 MAR 69



CO3O4 634-43-1

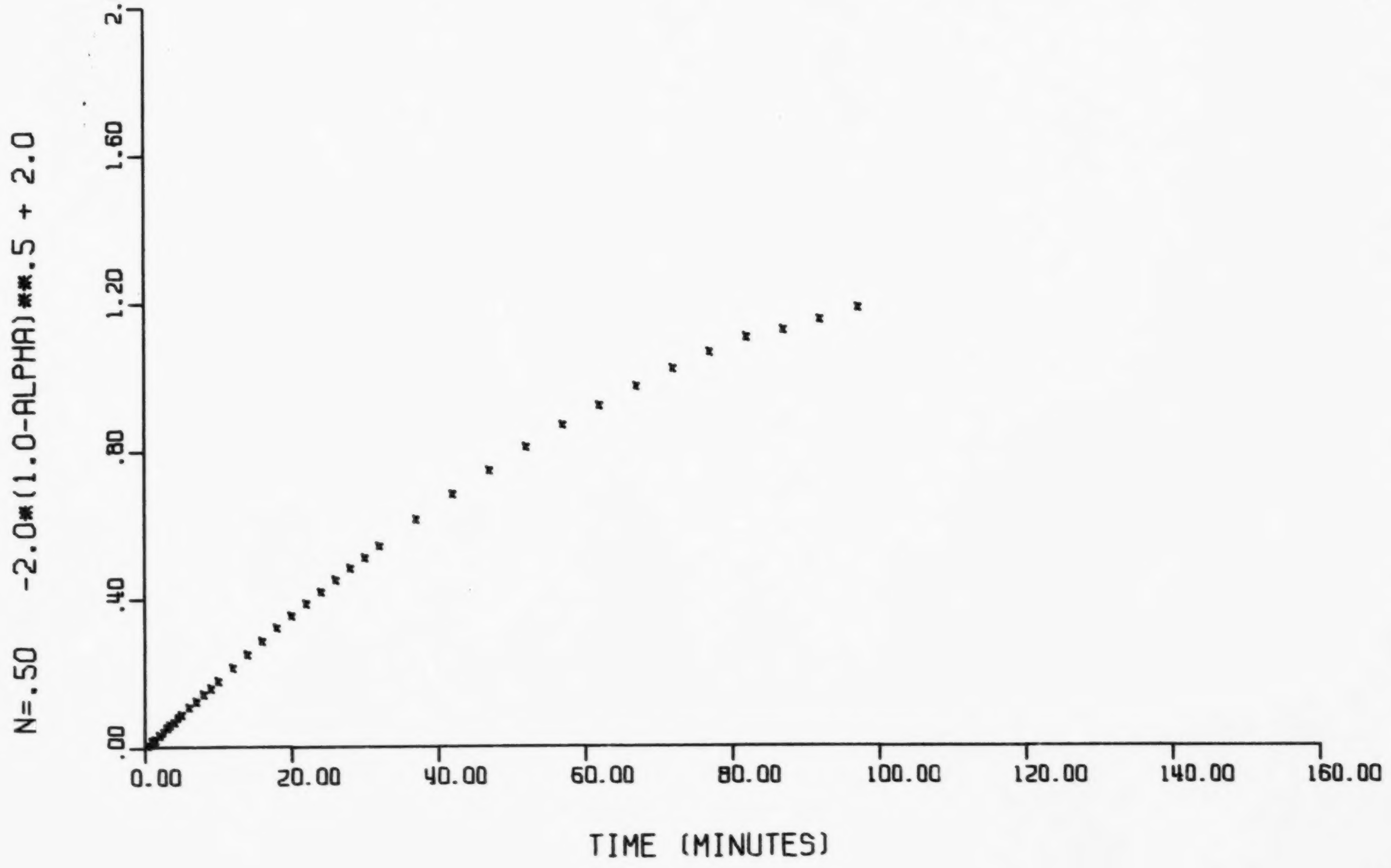
ISO-TGA-3 TEMP = 453 DEG C.

$w_o/m_o=0.38$

31 MAR 69

TRACOR

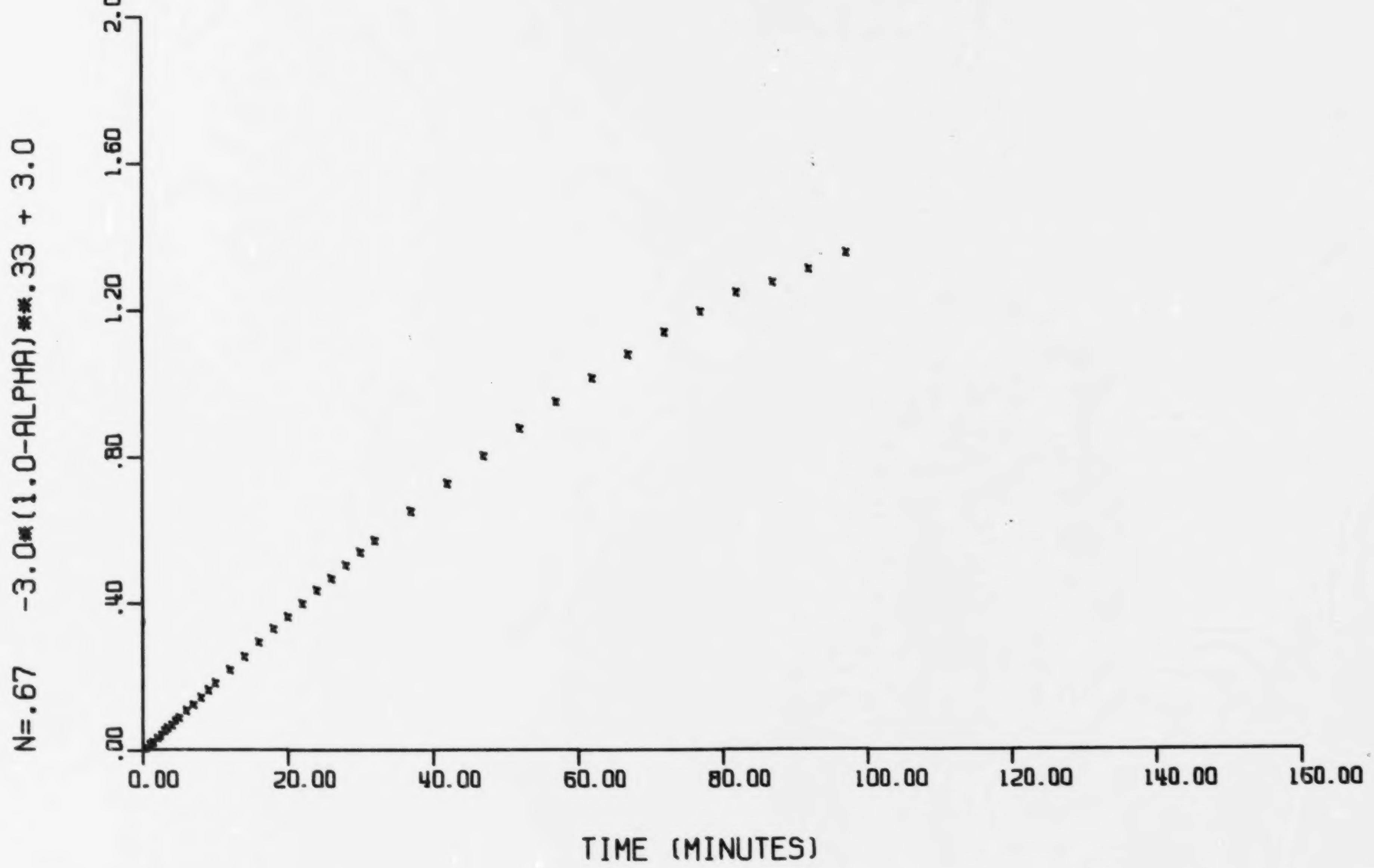
CO304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.
$w_o/m_o=0.38$



31 MAR 69

TRACOR

CO304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.
$w_o/m_o=0.38$

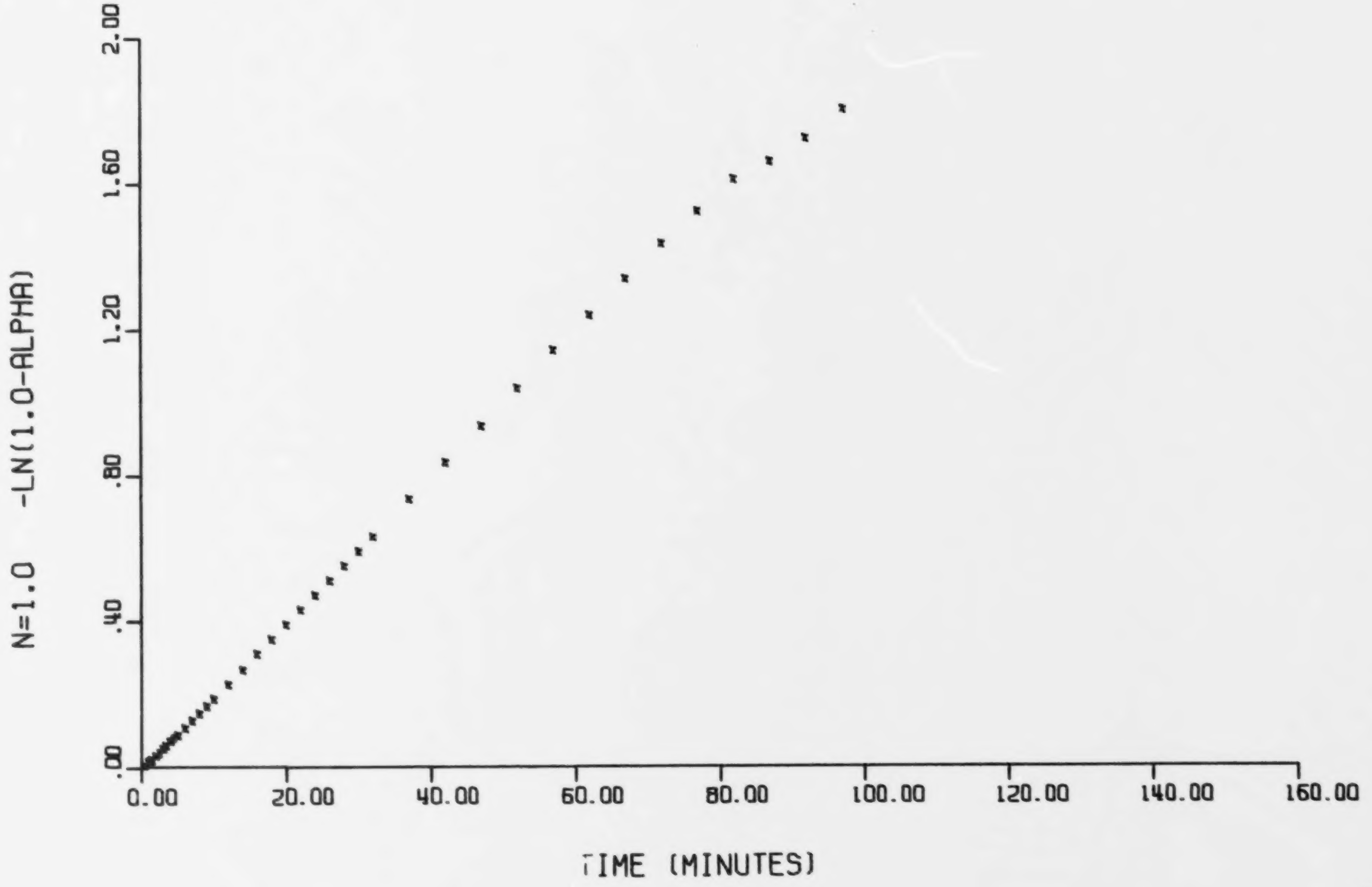


31 MAR 69

CO3O4 634-43-1

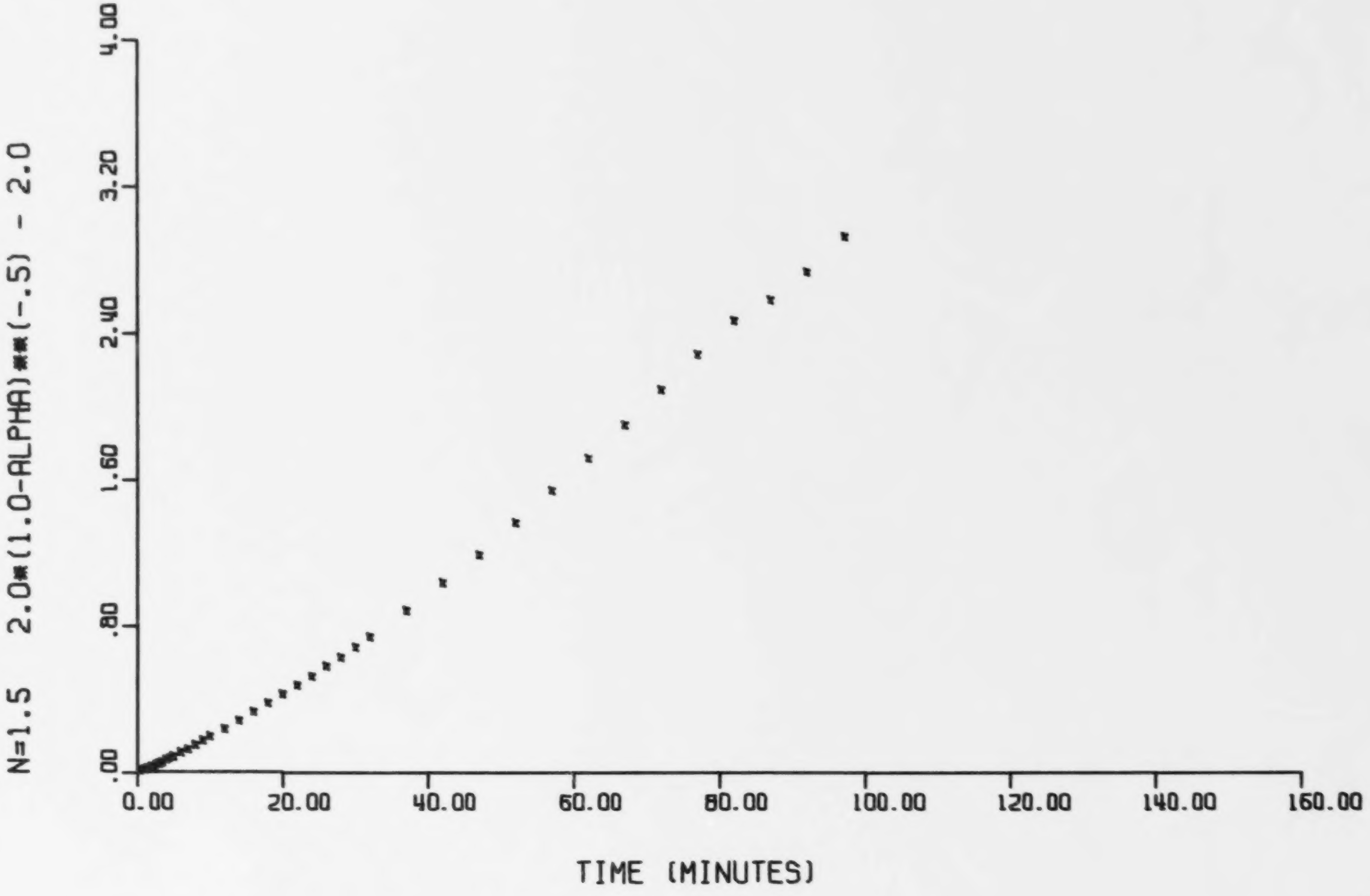
ISO-TGA-3 TEMP = 453 DEG C.

$w_o/m_o=0.38$



31 MAR 69

CO304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.
w_o/m_o=0.38

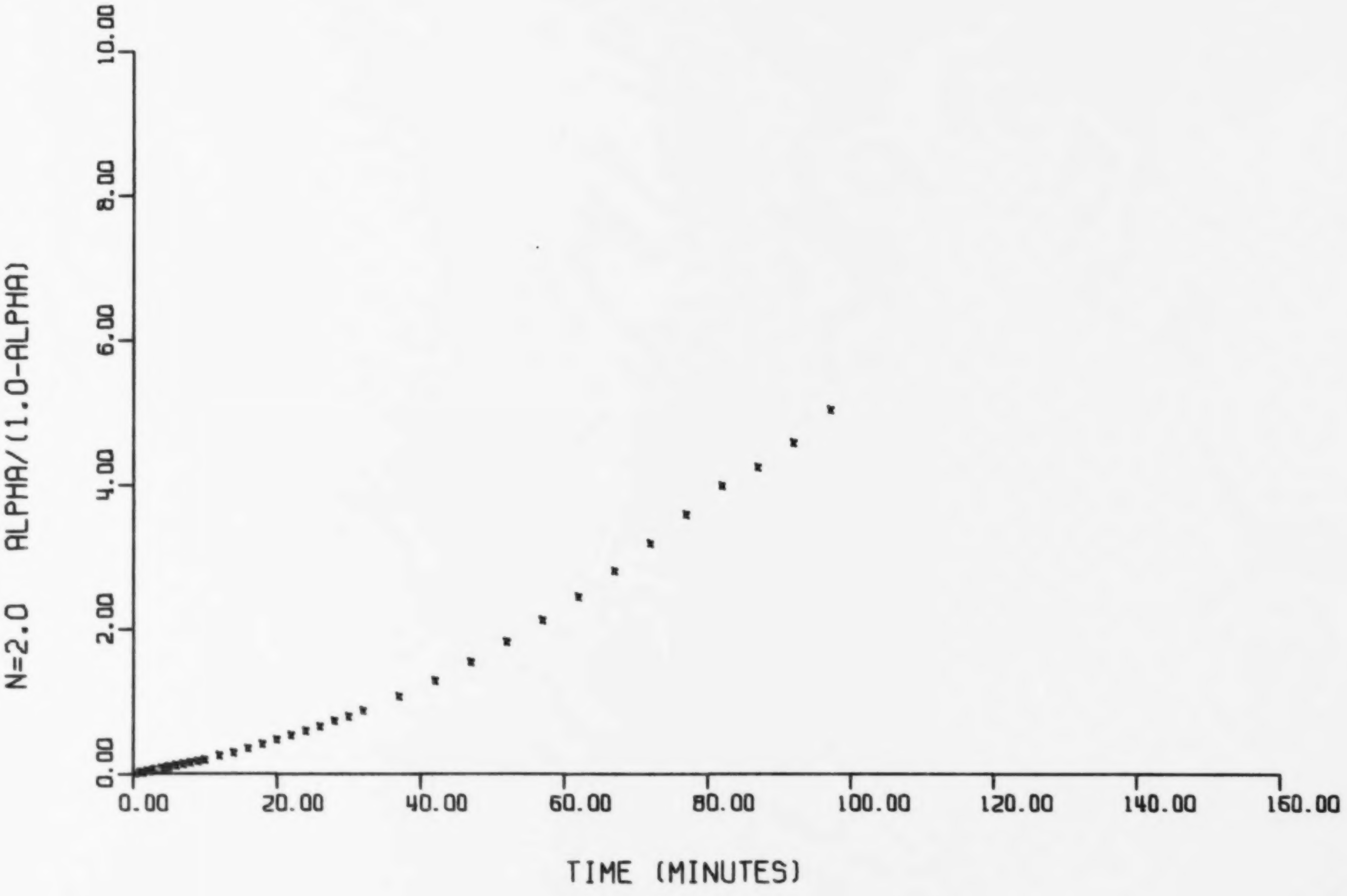


31 MAR 69

CO3O4 634-43-1

ISO-TGA-3 TEMP = 453 DEG C.

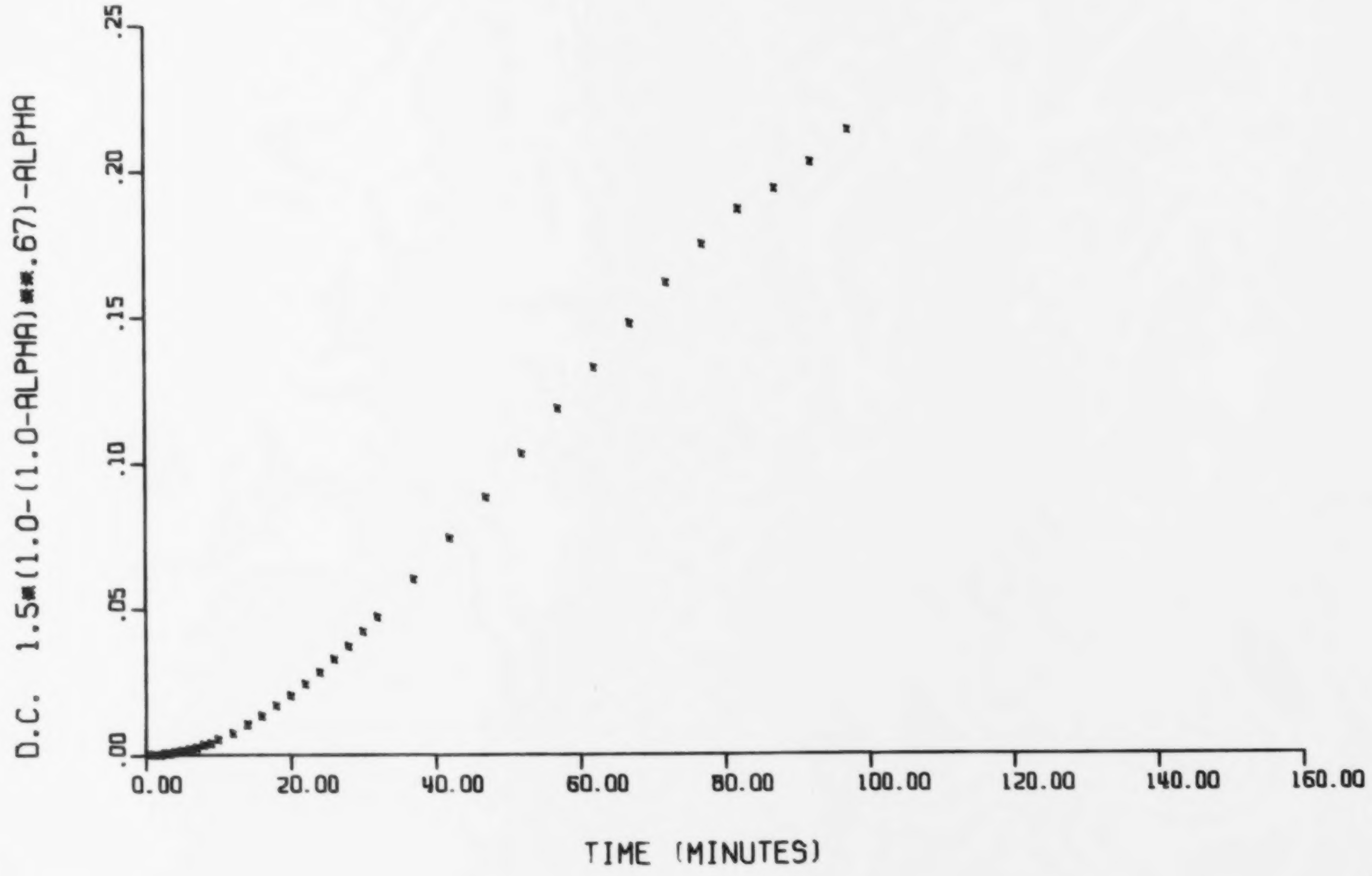
$w_o/m_o = 0.38$



31 MAR 69

TRACOR

C0304 634-43-1
ISO-TGA-3 TEMP = 453 DEG C.
$w_o/m_o=0.38$



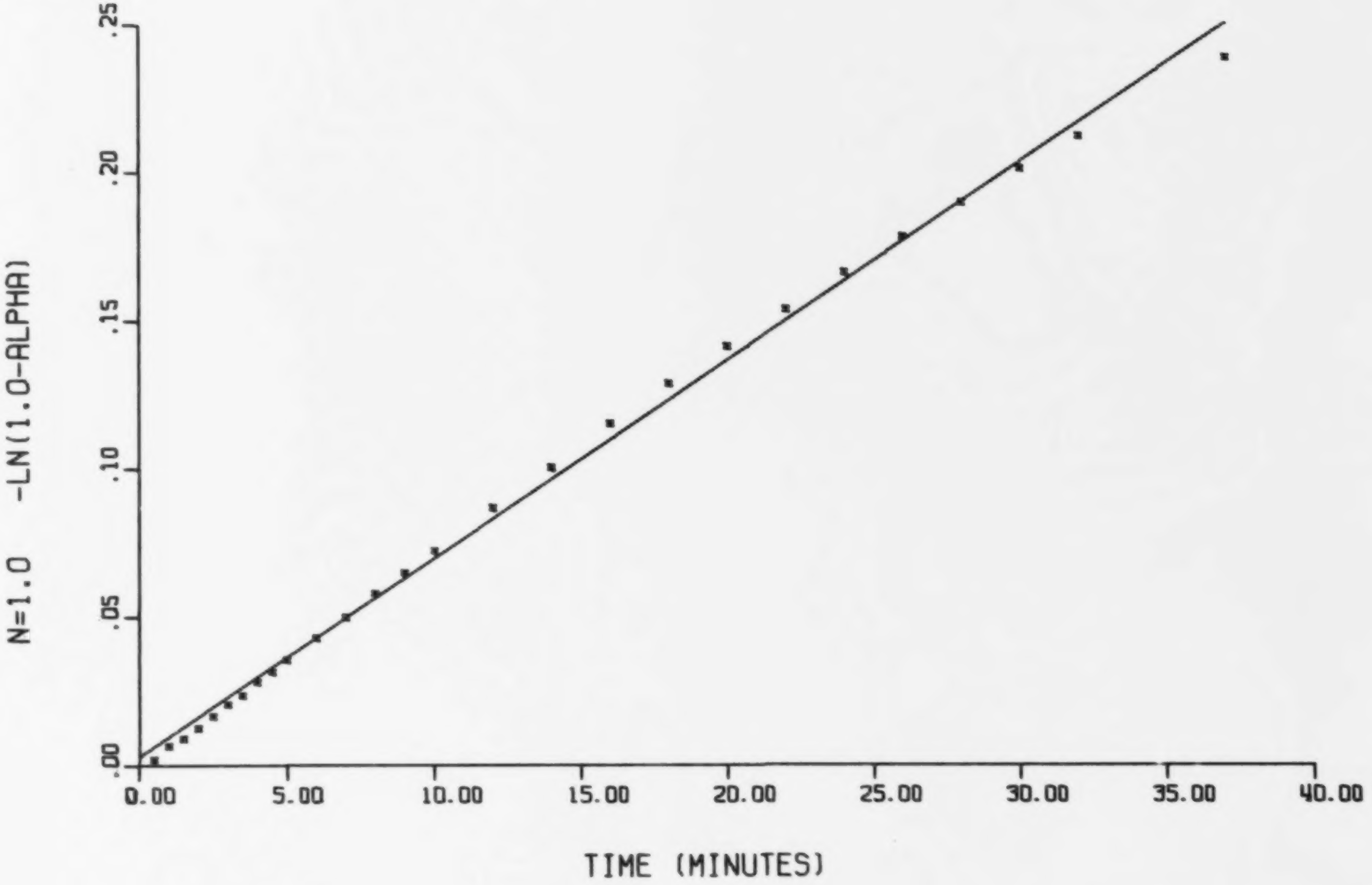
31 MAR 69

TRACOR

C0304 634-43-1

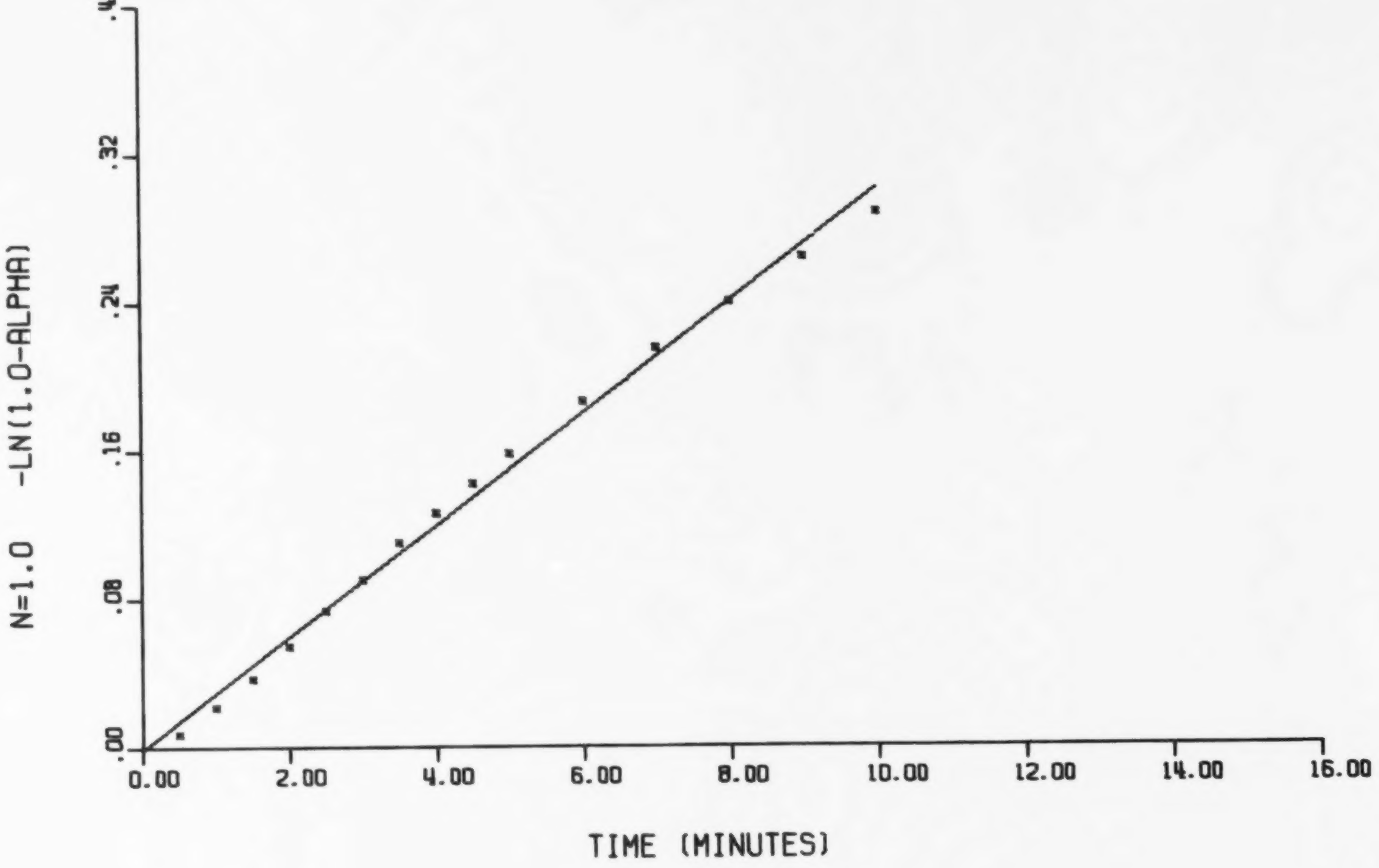
ISO-TGA-3 TEMP = 453 DEG C.

$w_o/m_o=0.931$



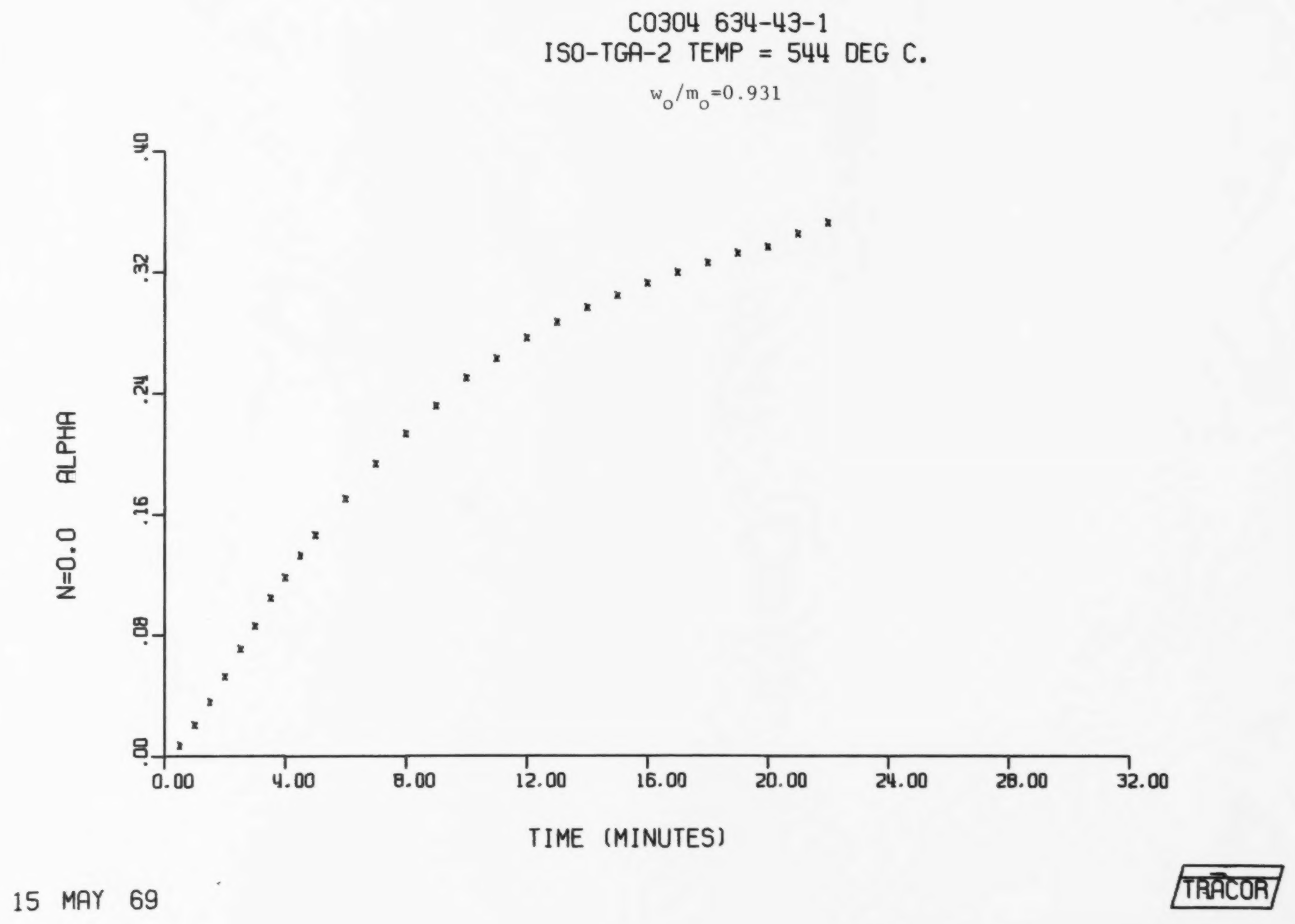
20 MAY 69

C0304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
$w_o/m_o=0.931$



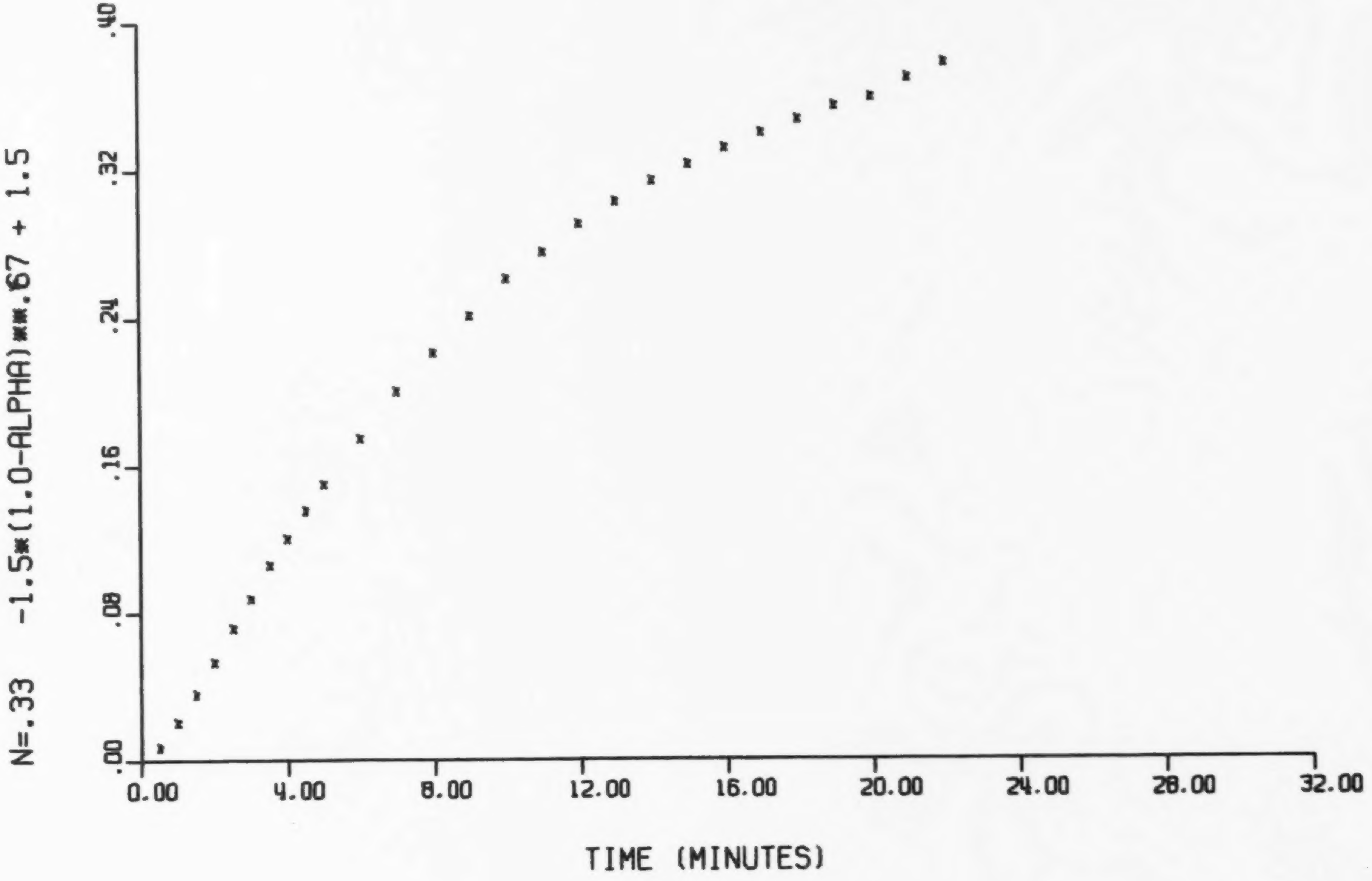
20 MAY 69

TRACOR


C0304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
w_o/m_o=0.931
N=0.0 ALPHA
.00
.08
.16
.24
.32
.40
0.00
4.00
8.00
12.00
16.00
20.00
24.00
28.00
32.00
TIME (MINUTES)
15 MAY 69
TRACOR

C0304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.

$w_o/m_o=0.931$

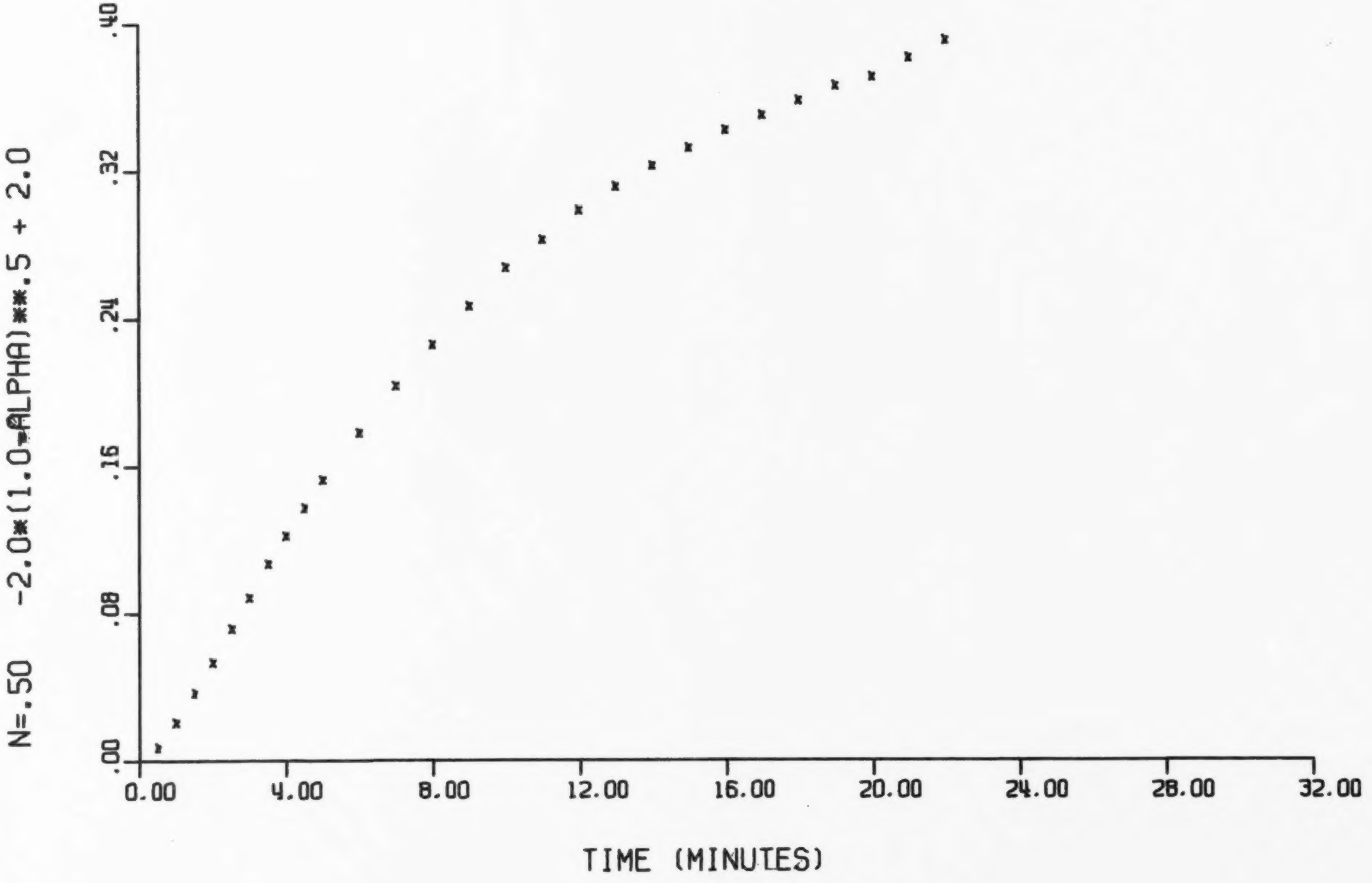


15 MAY 69

TRACOR

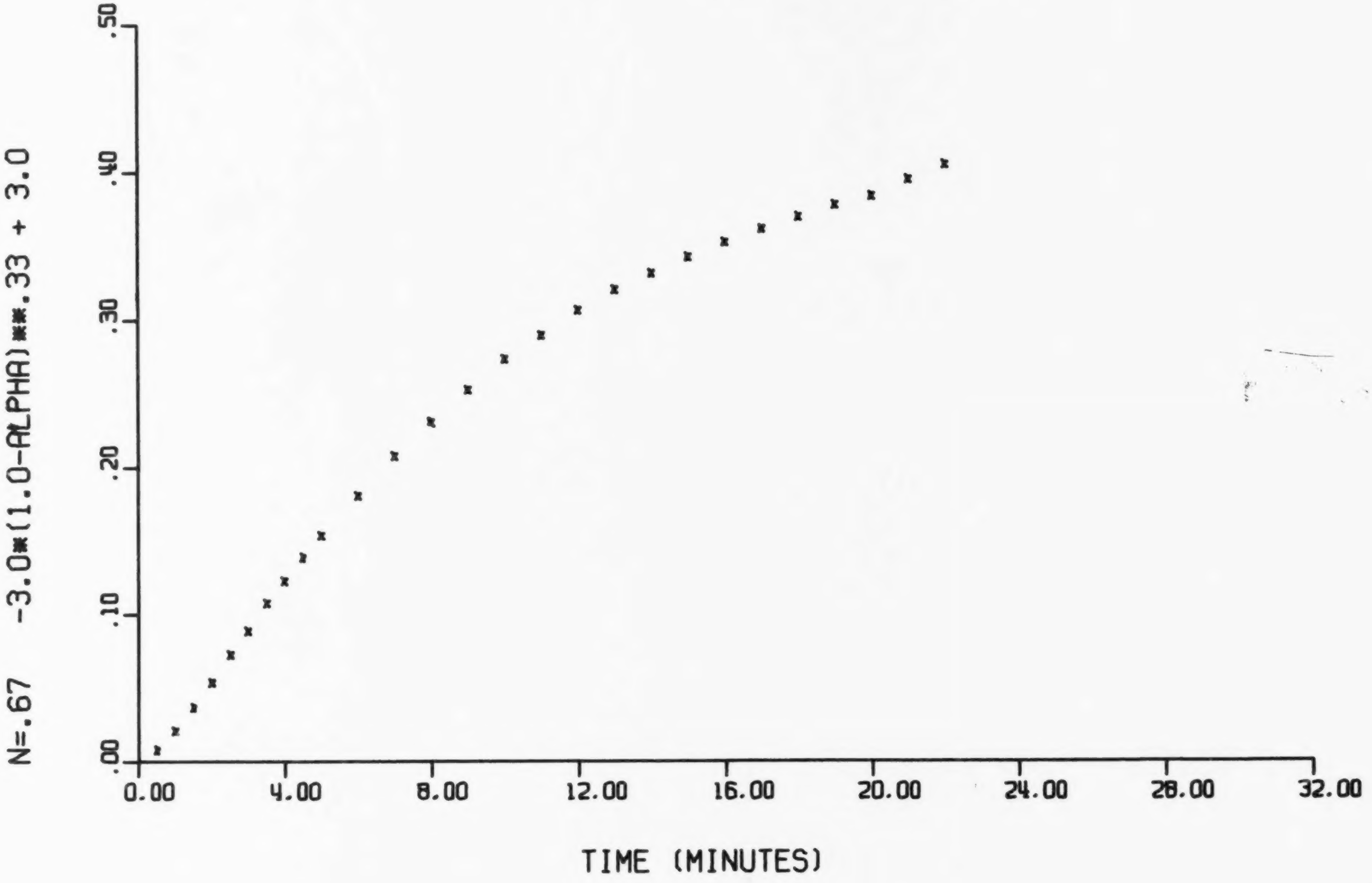
CO304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.

$w_o/m_o=0.931$



15 MAY 69

TRACOR

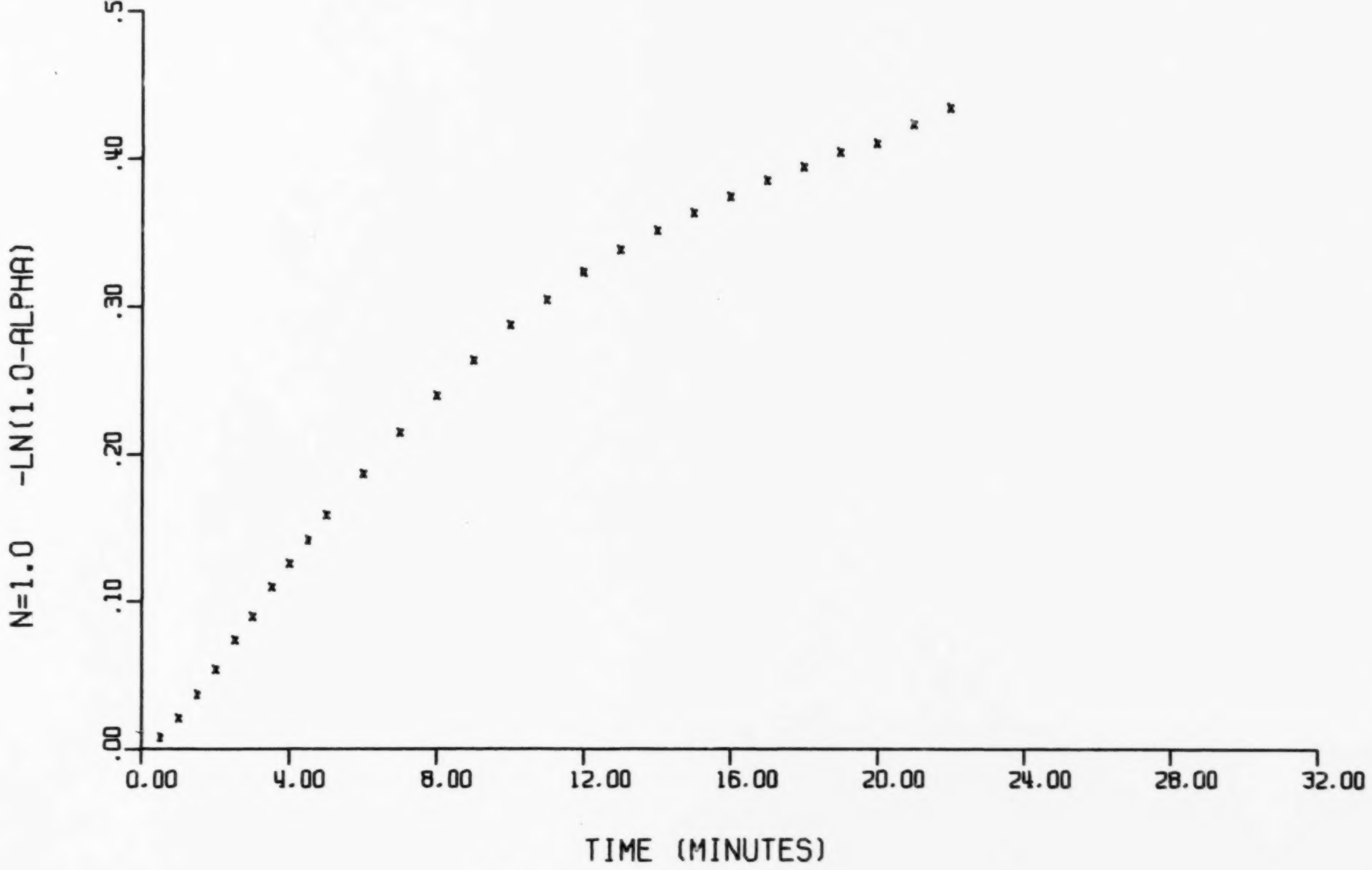

CO304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.

$w_o/m_o=0.931$

15 MAY 69

TRACOR

CO3O4 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
$w_o/m_o=0.931$



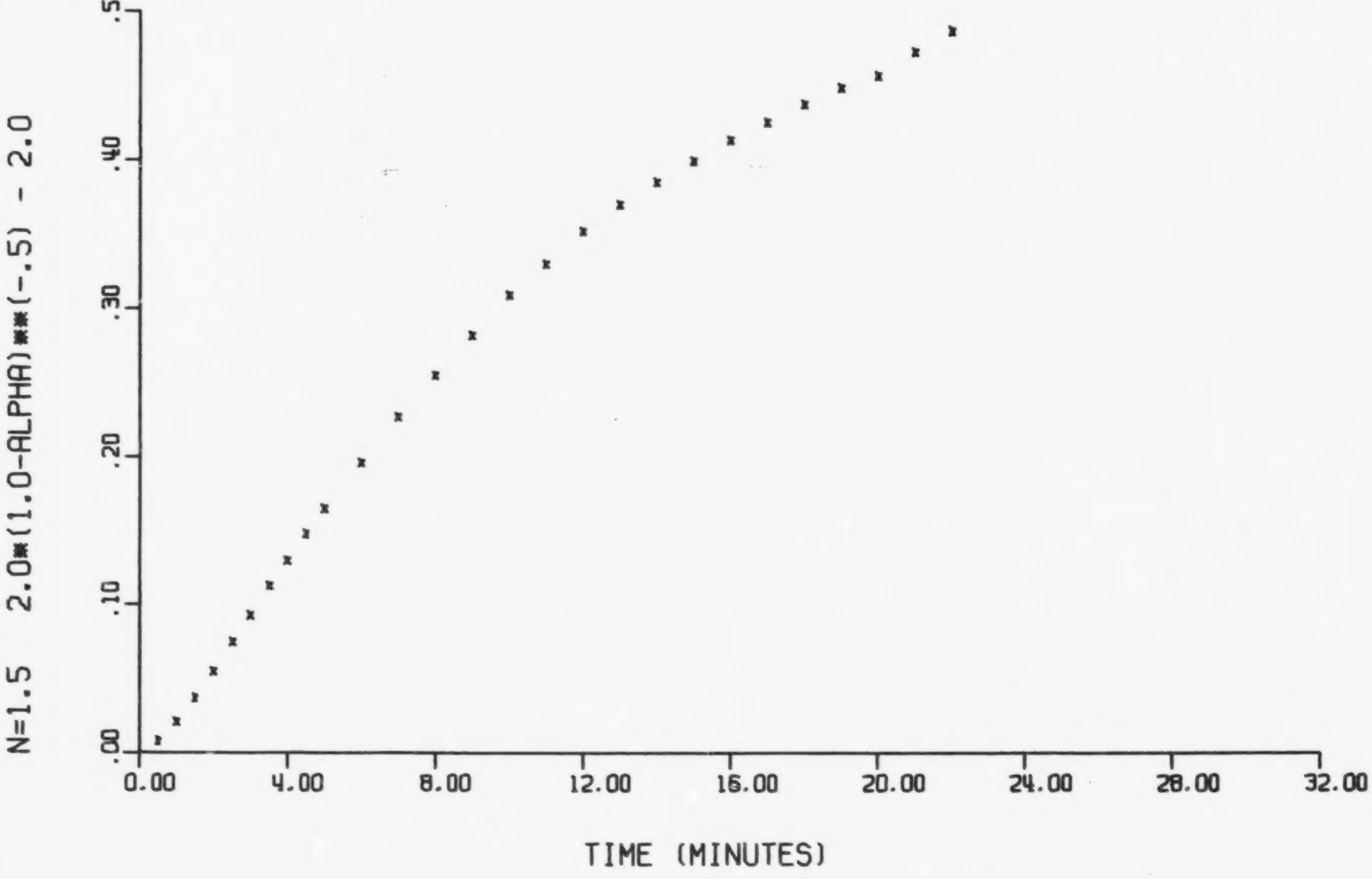
15 MAY 69

TRACOR

CO304 634-43-1

ISO-TGA-2 TEMP = 544 DEG C.

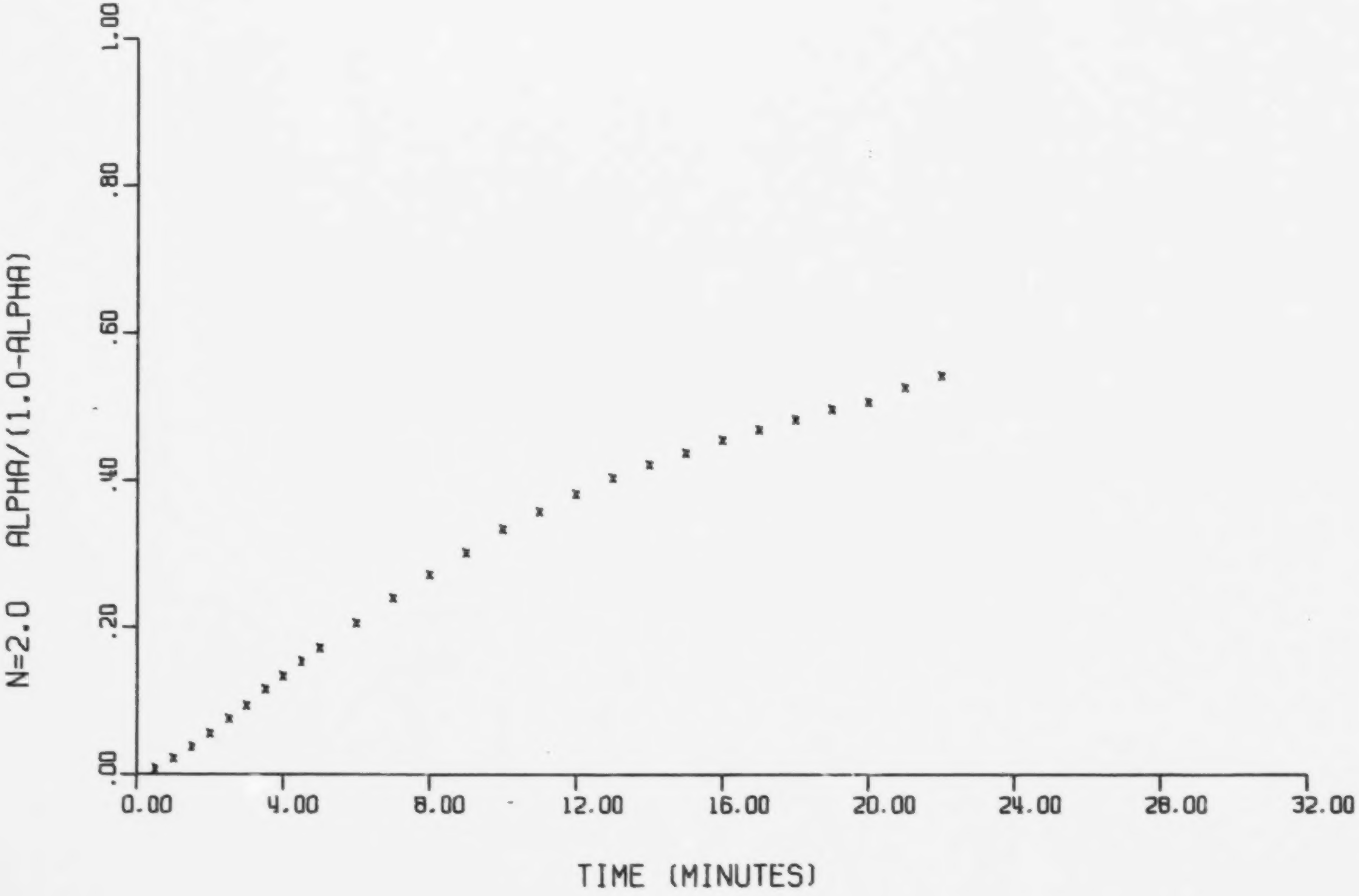
$w_o/m_o=0.931$



15 MAY 69

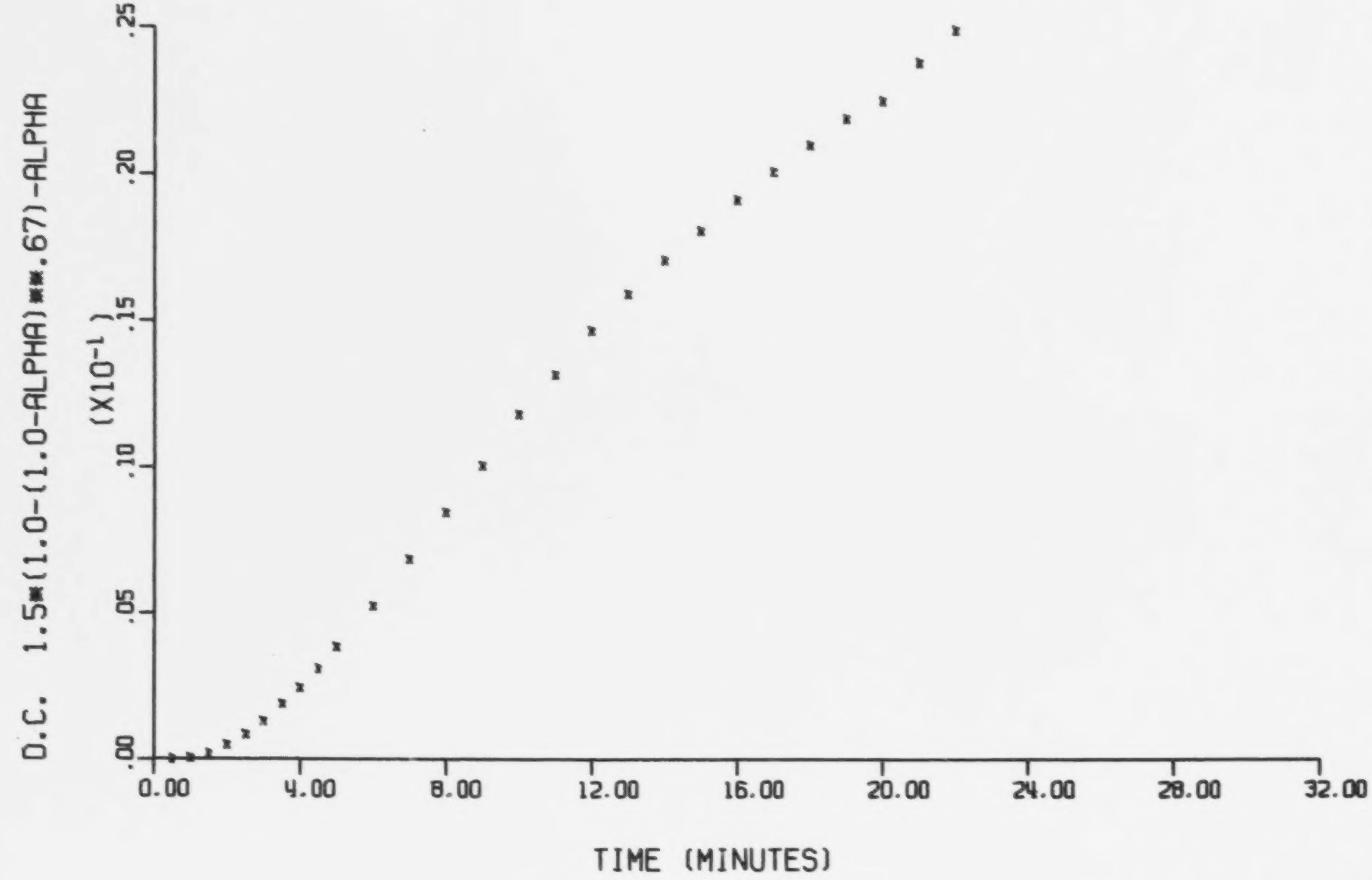
TRACOR

CO304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
$w_o/m_o=0.931$



15 MAY 69

CO304 634-43-1
ISO-TGA-2 TEMP = 544 DEG C.
$w_o/m_o=0.931$

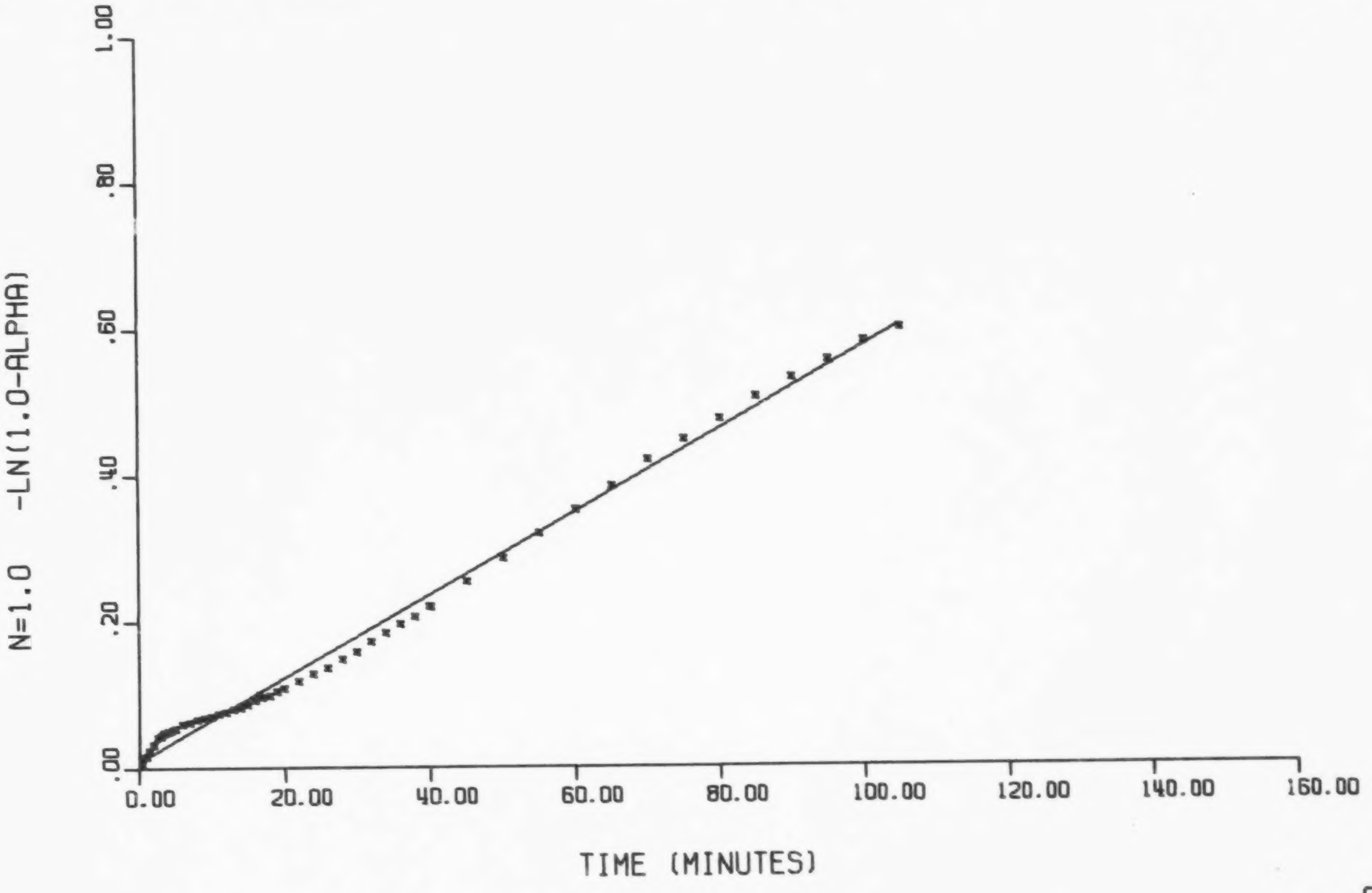


15 MAY 69

CO304 634-71-2

ISO TGA 1 TEMP = 359 DEG C

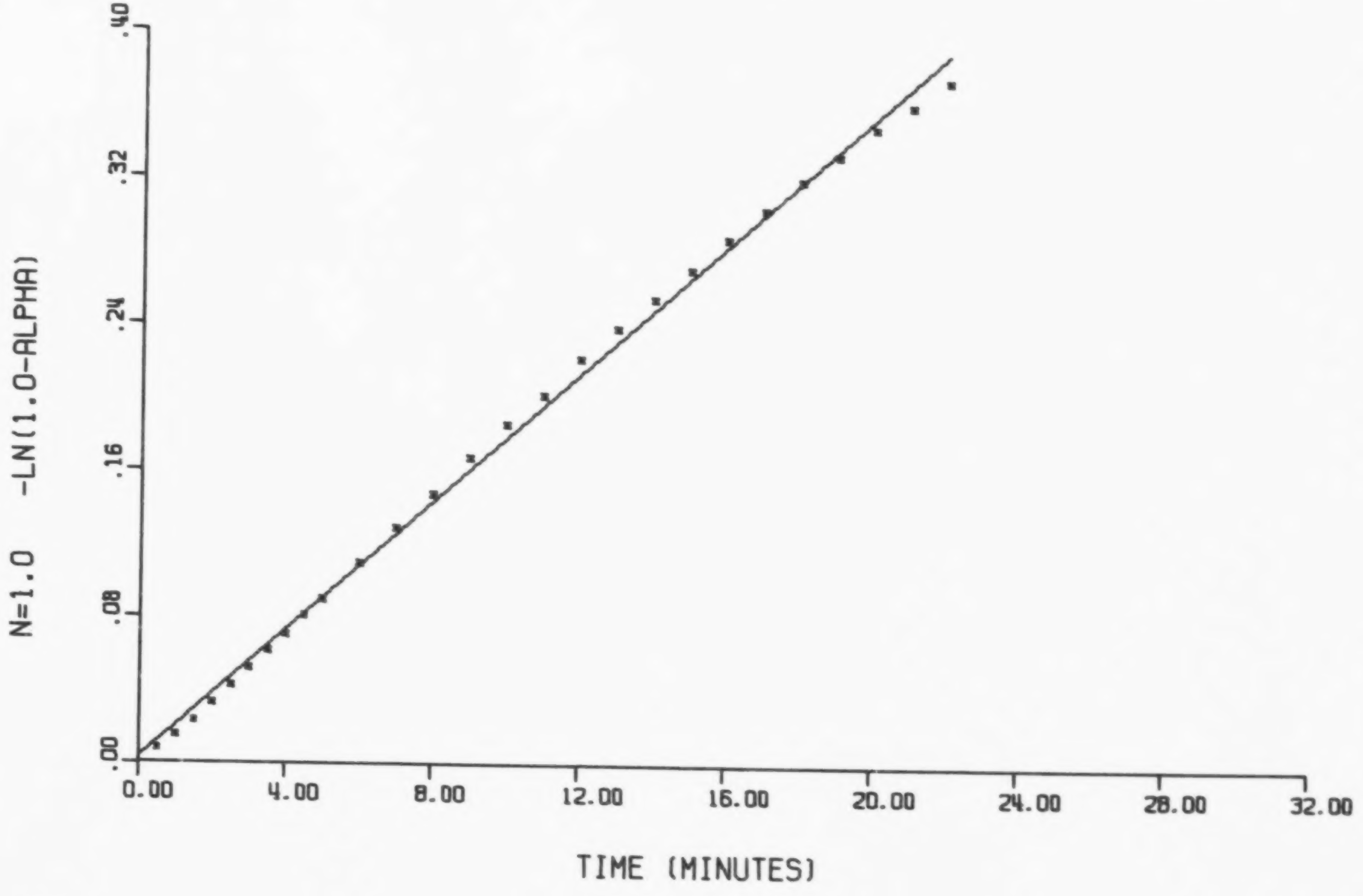
w_o/m_o=0.931



20 MAY 69

TRACOR

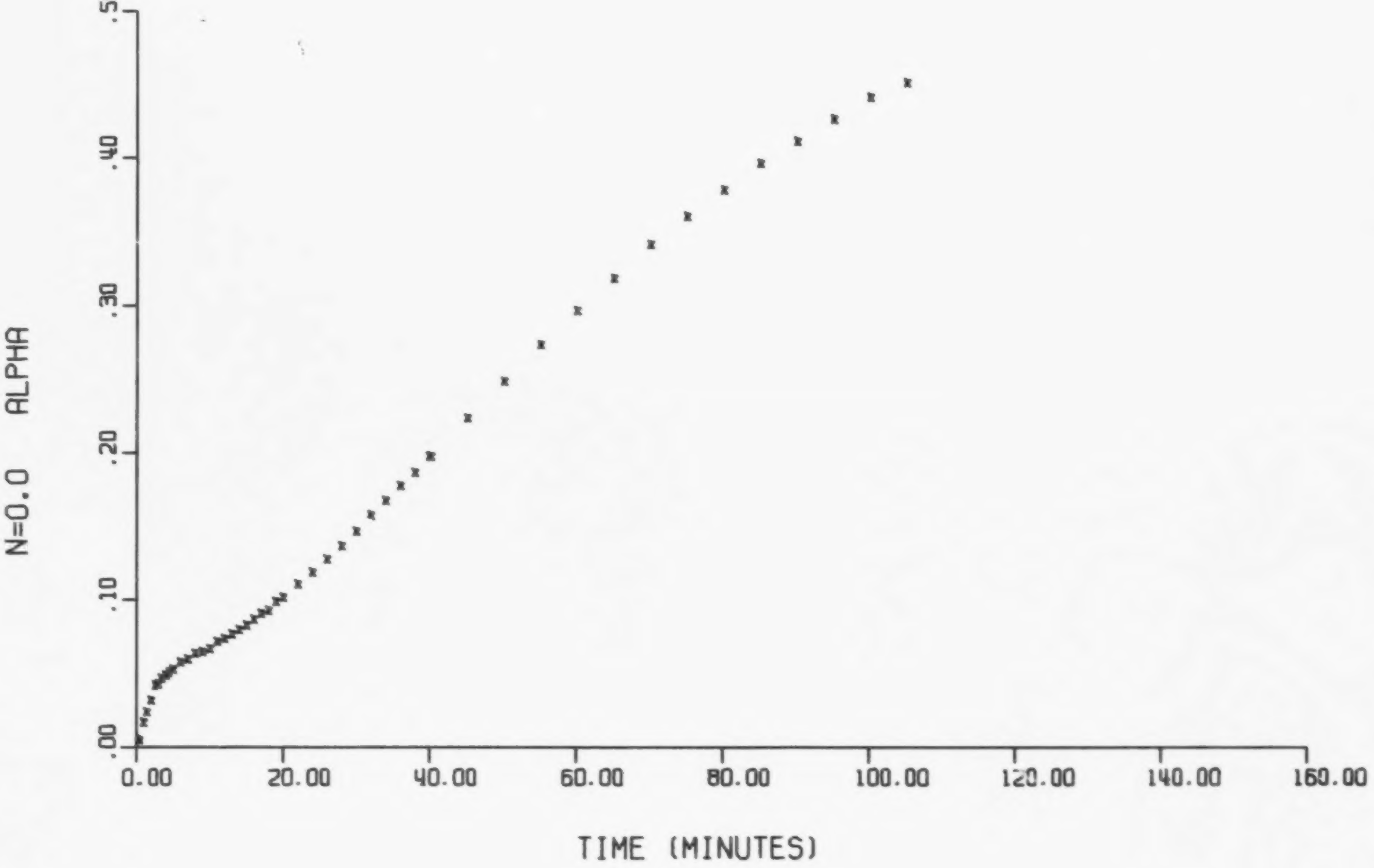
C0304 634-71-2
ISO TGA 2 TEMP = 430 DEG C
$w_o/m_o=0.931$



20 MAY 69

TRACOR

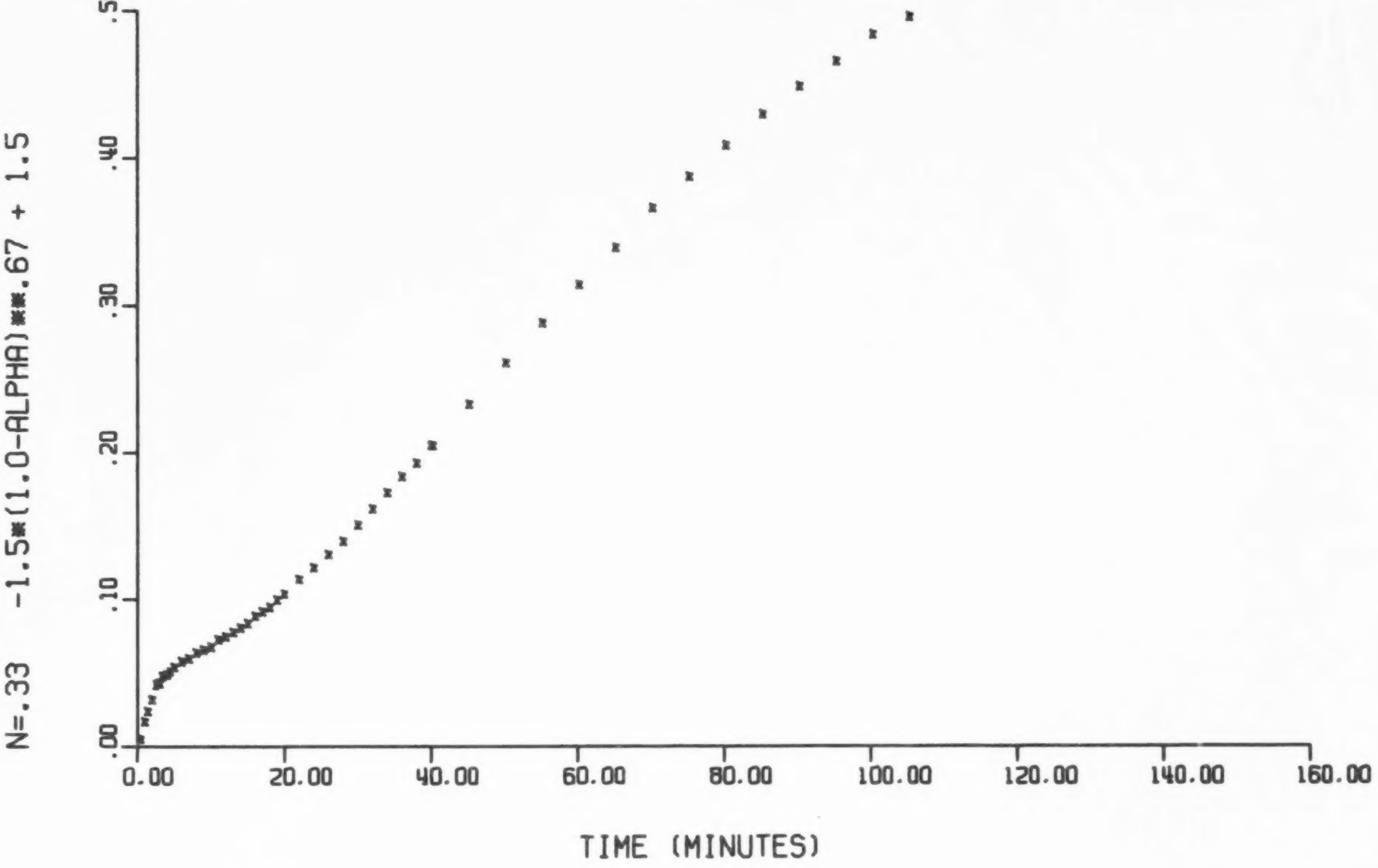
CO304 634-71-2
ISO TGA 1 TEMP = 359 DEG C
$w_o/m_o=0.931$



15 MAY 69

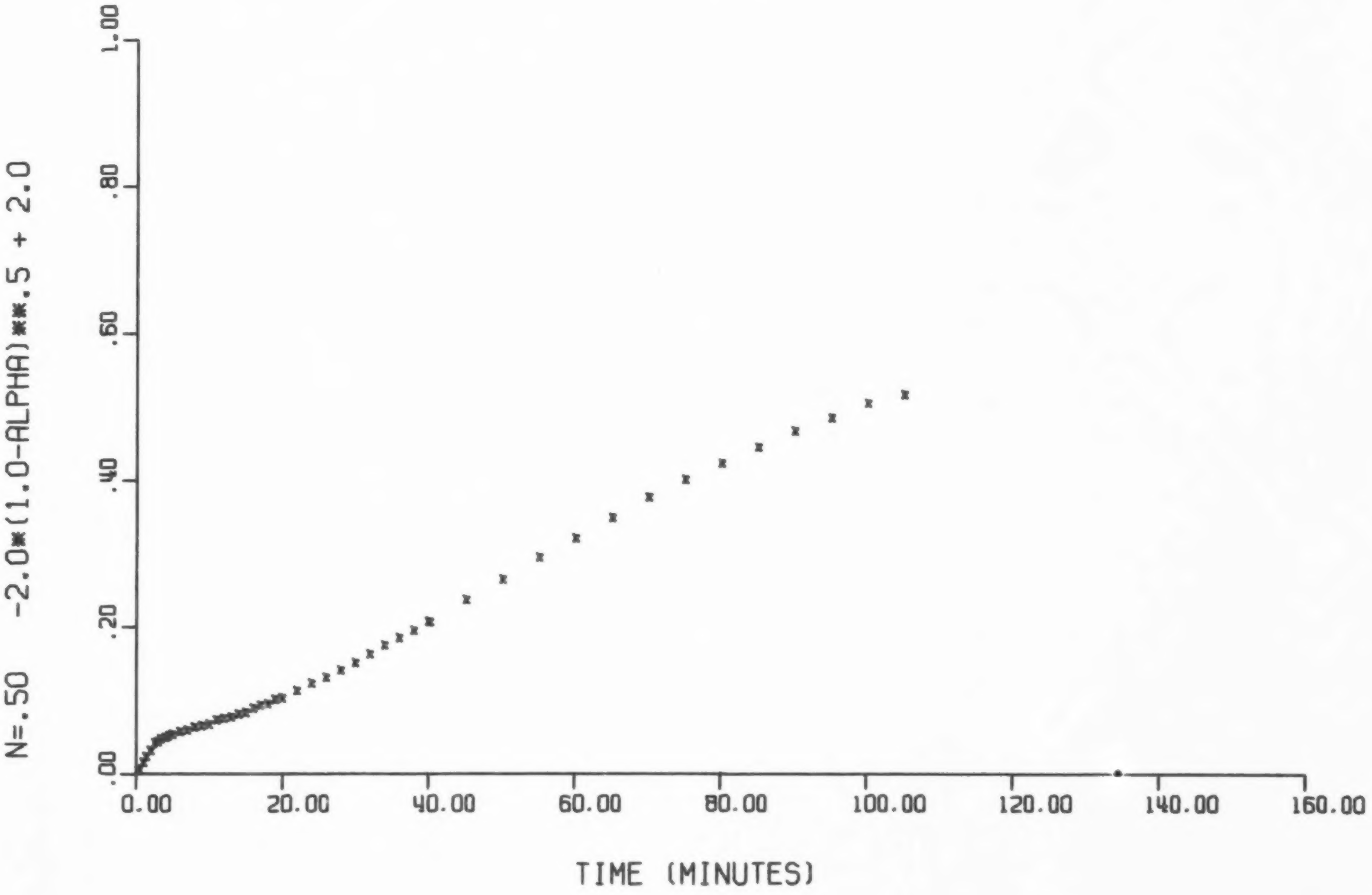
TRACOR

C0304 634-71-2
ISO TGA 1 TEMP = 359 DEG C
$w_o/m_o=0.931$



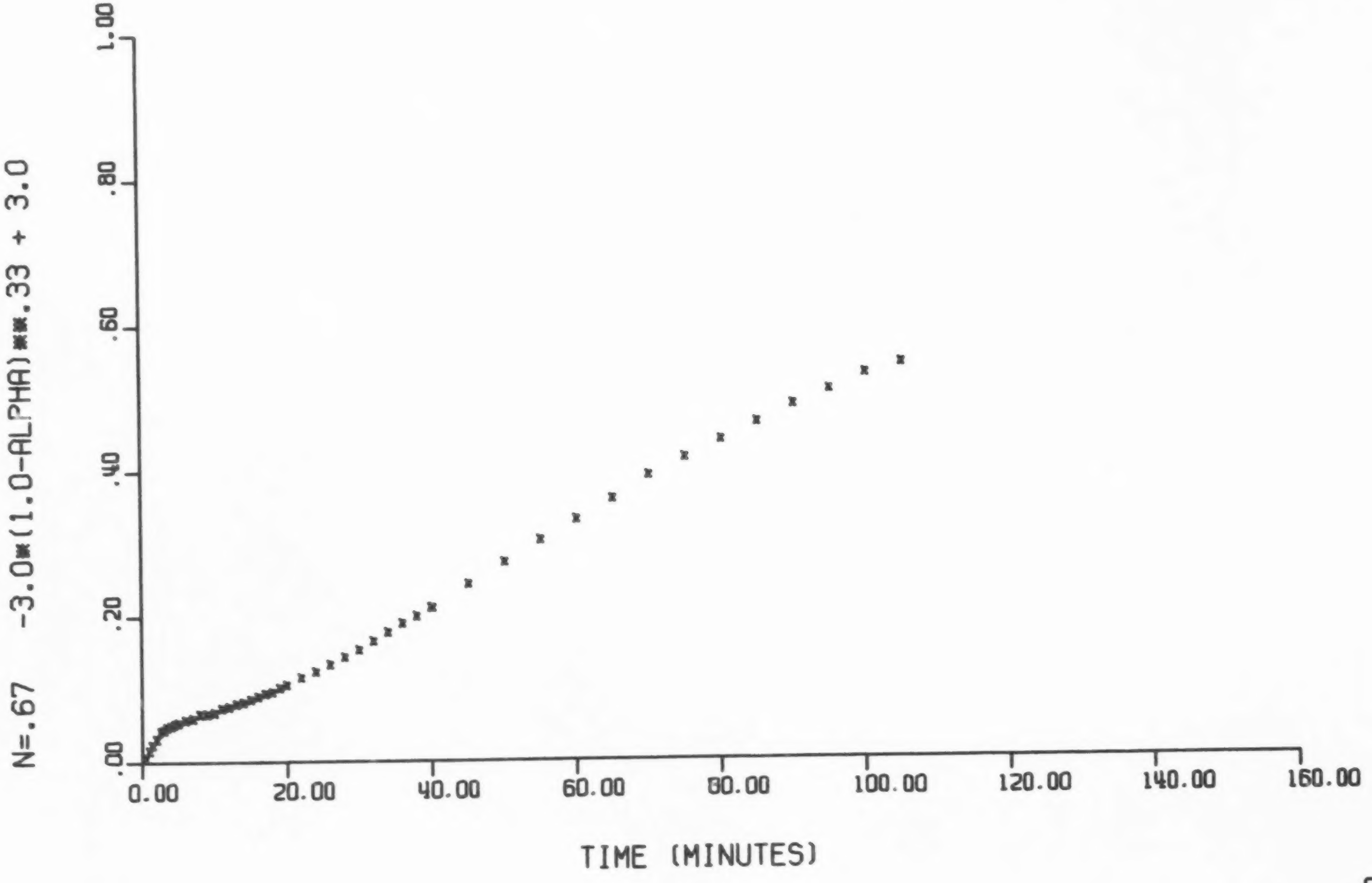
15 MAY 69

CO304 634-71-2
ISO TGA 1   TEMP = 359 DEG C
$w_o/m_o=0.931$



15 MAY 69

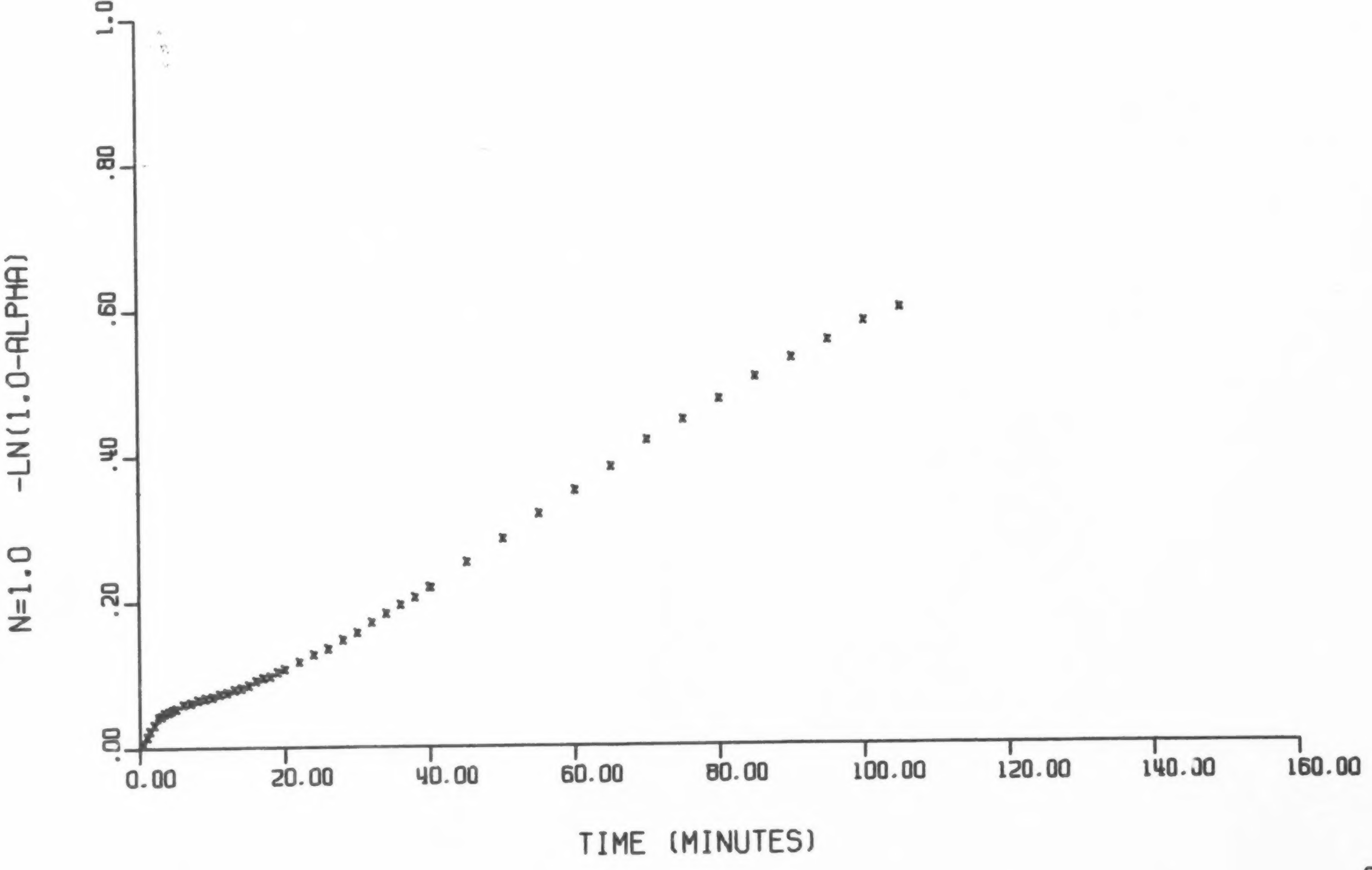
CO304 634-71-2
ISO TGA 1   TEMP = 359 DEG C
$w_o/m_o=0.931$



15 MAY 69

TRACOR

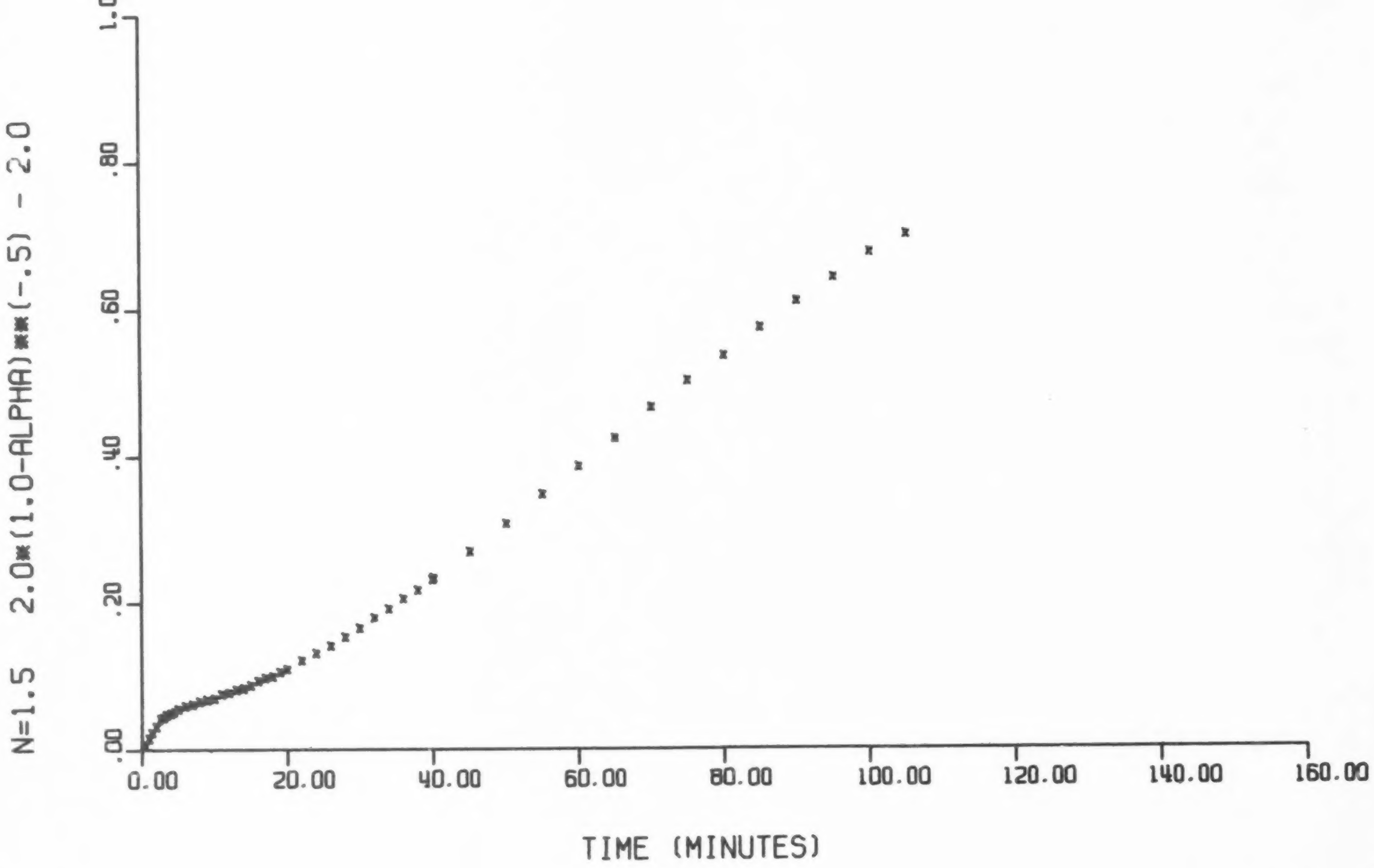
CO3O4 634-71-2
ISO TGA 1 TEMP = 359 DEG C
$w_o/m_o=0.931$



15 MAY 69

TRACOR

C0304 634-71-2
ISO TGA 1 TEMP = 359 DEG C
$w_o/m_o=0.931$

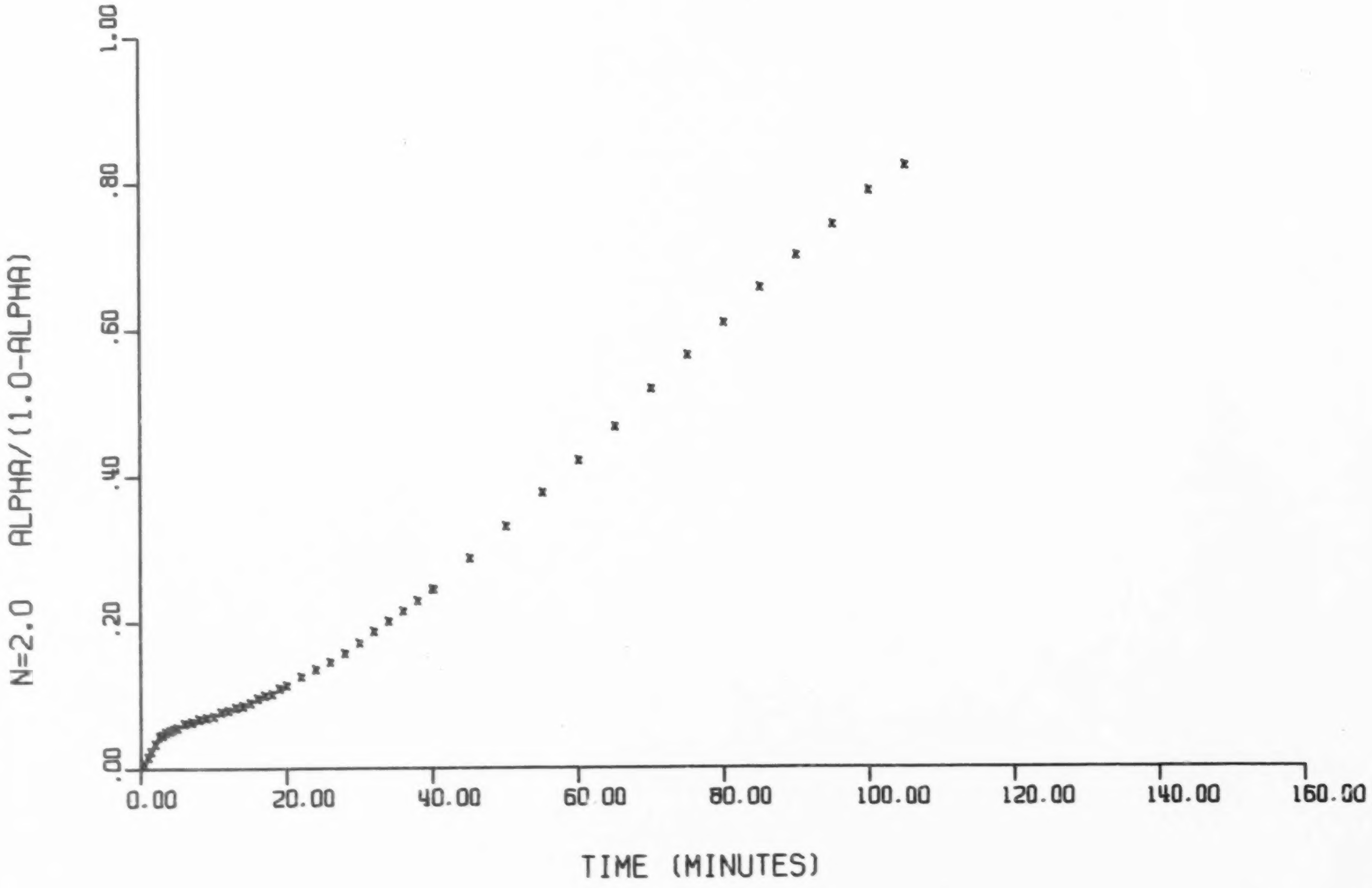


15 MAY 69

TRACOR

CO304 634-71-2
ISO TGA 1   TEMP = 359 DEG C

$w_o/m_o=0.931$



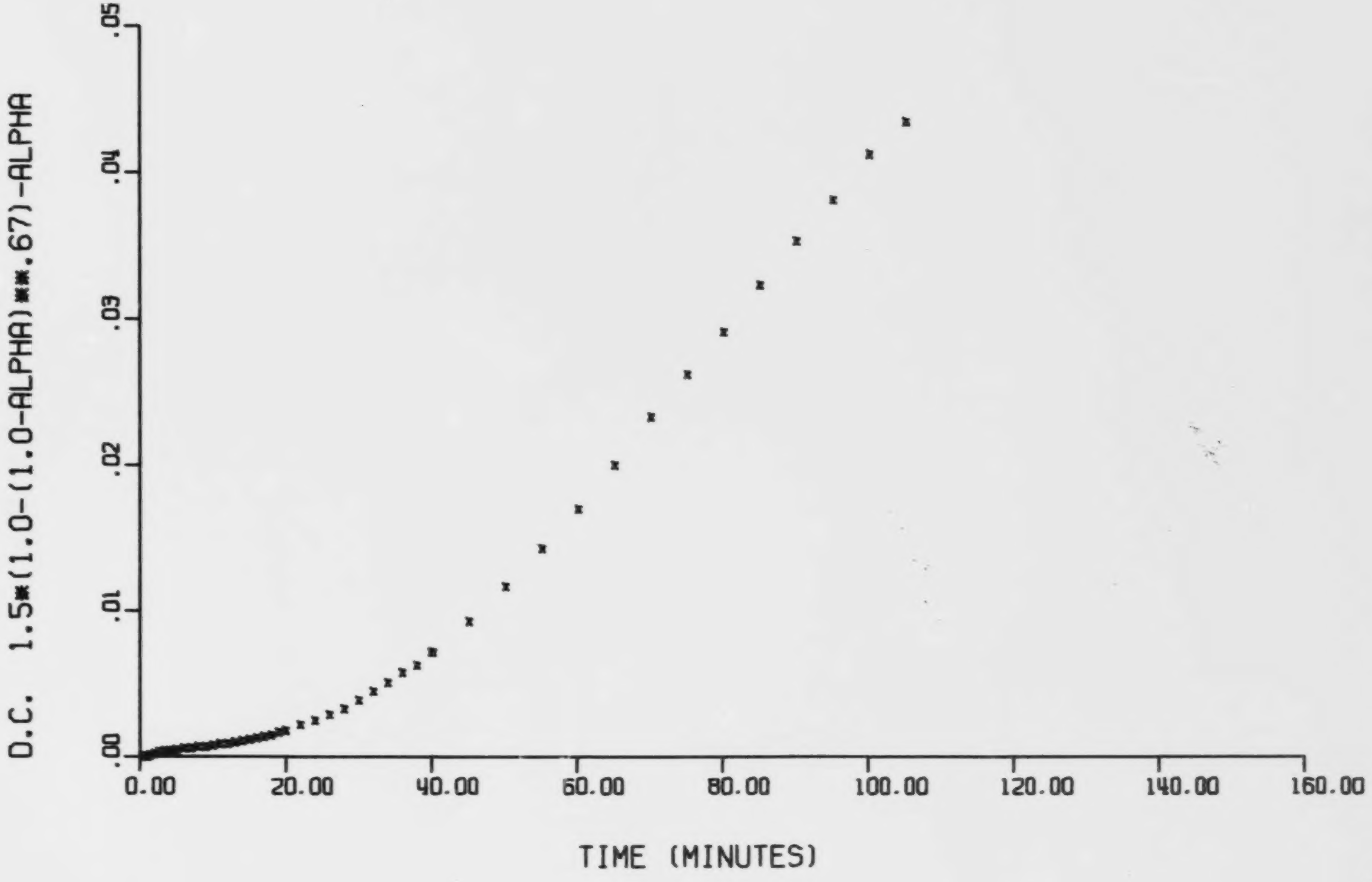
15 MAY 69

TRACOR

CO3O4 634-71-2

ISO TGA 1 TEMP = 359 DEG C

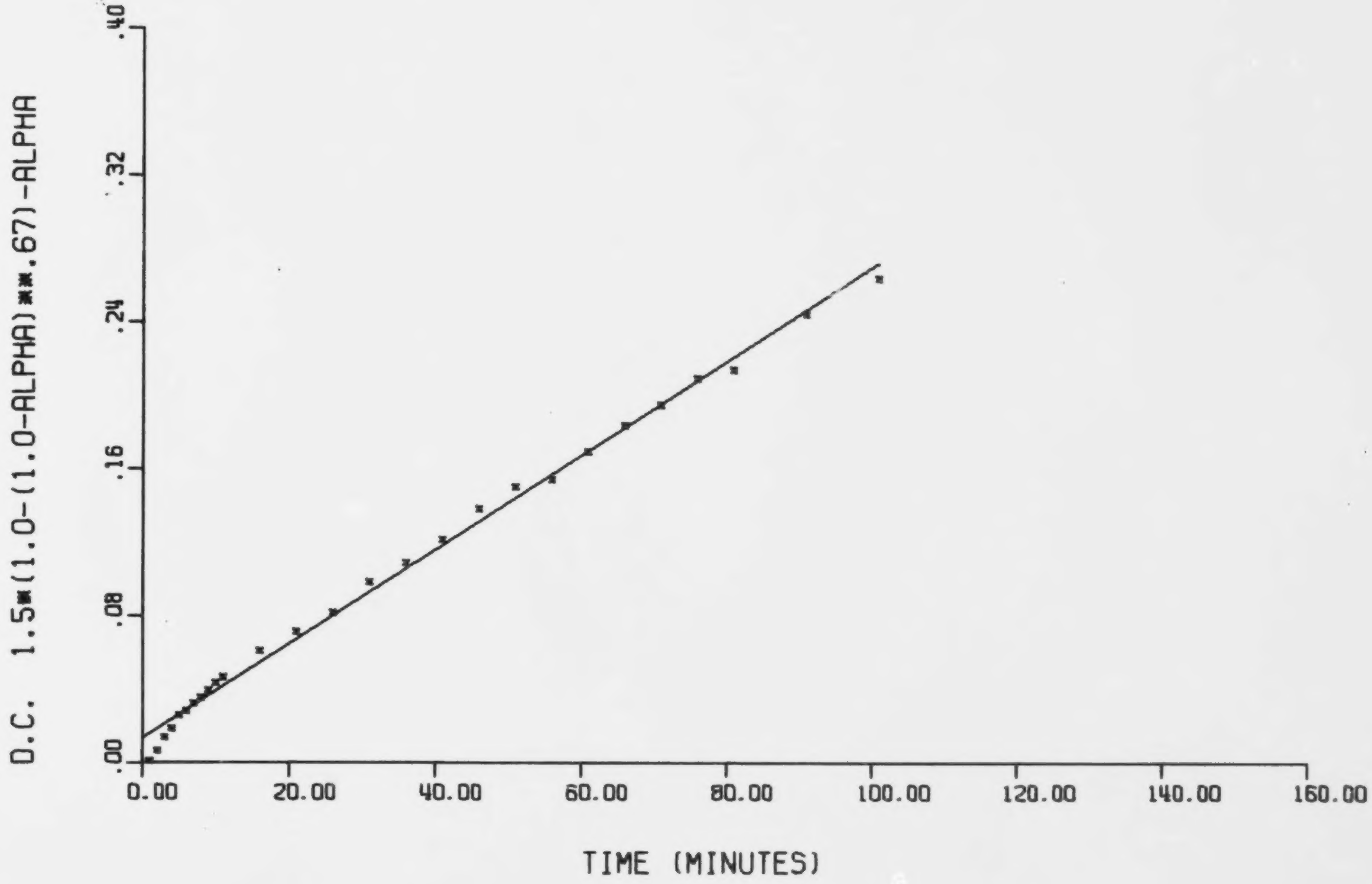
$w_o/m_o = 0.931$



15 MAY 69

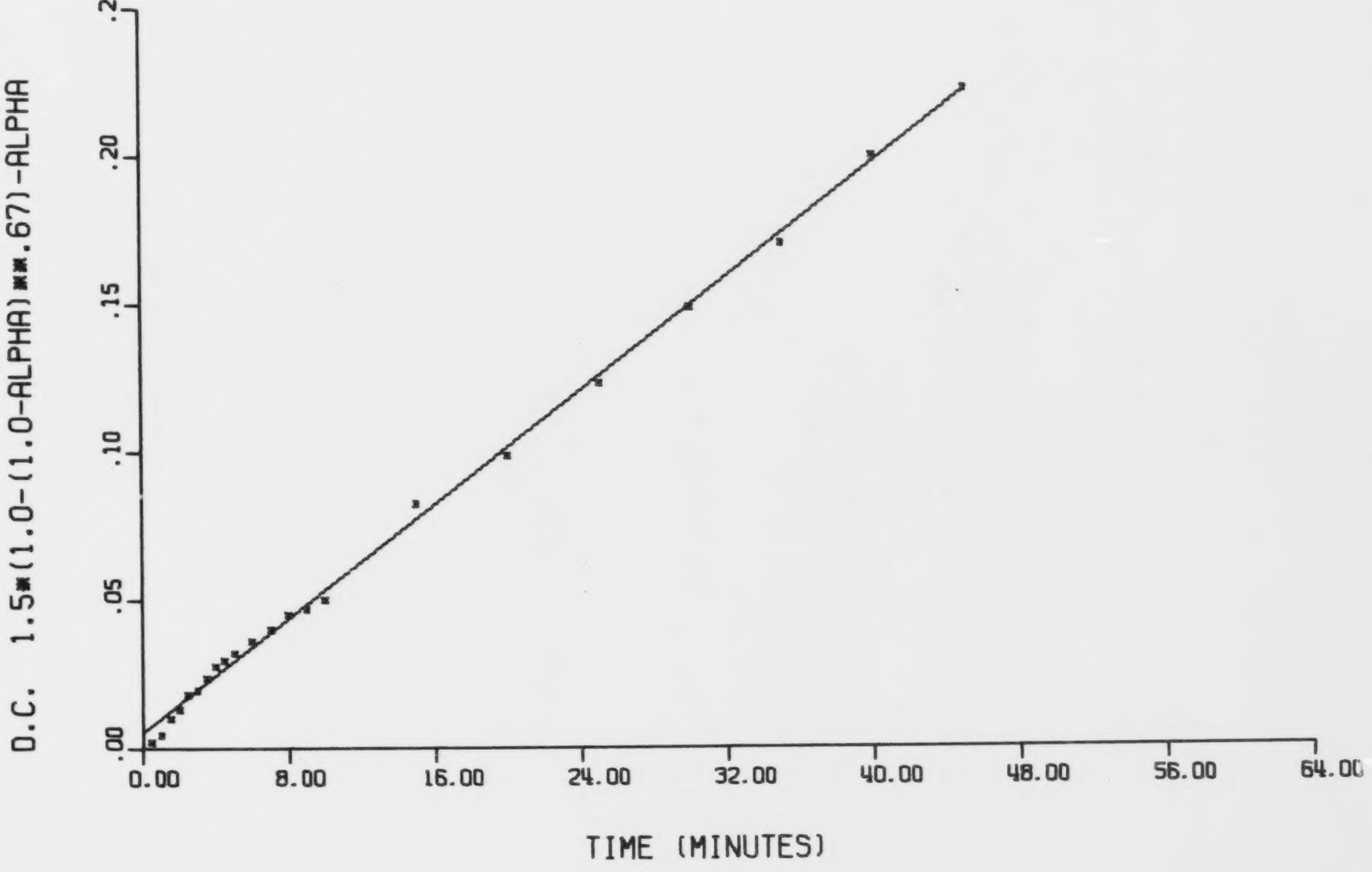
TRACOR

CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



14 APR 69

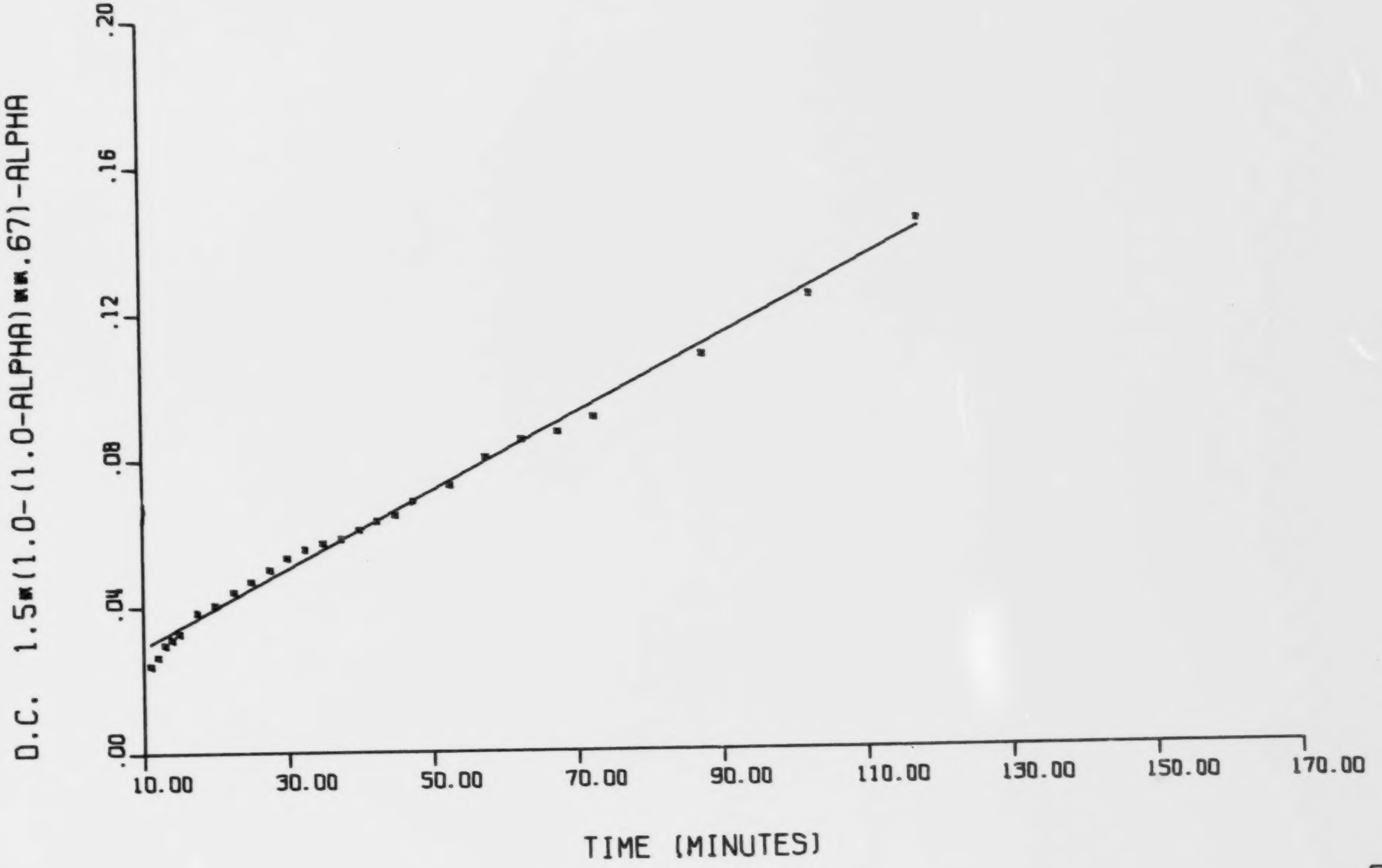
CR203 634-59-2
ISO-TGA-1 TEMP = 390 DEG C.



14 APR 69

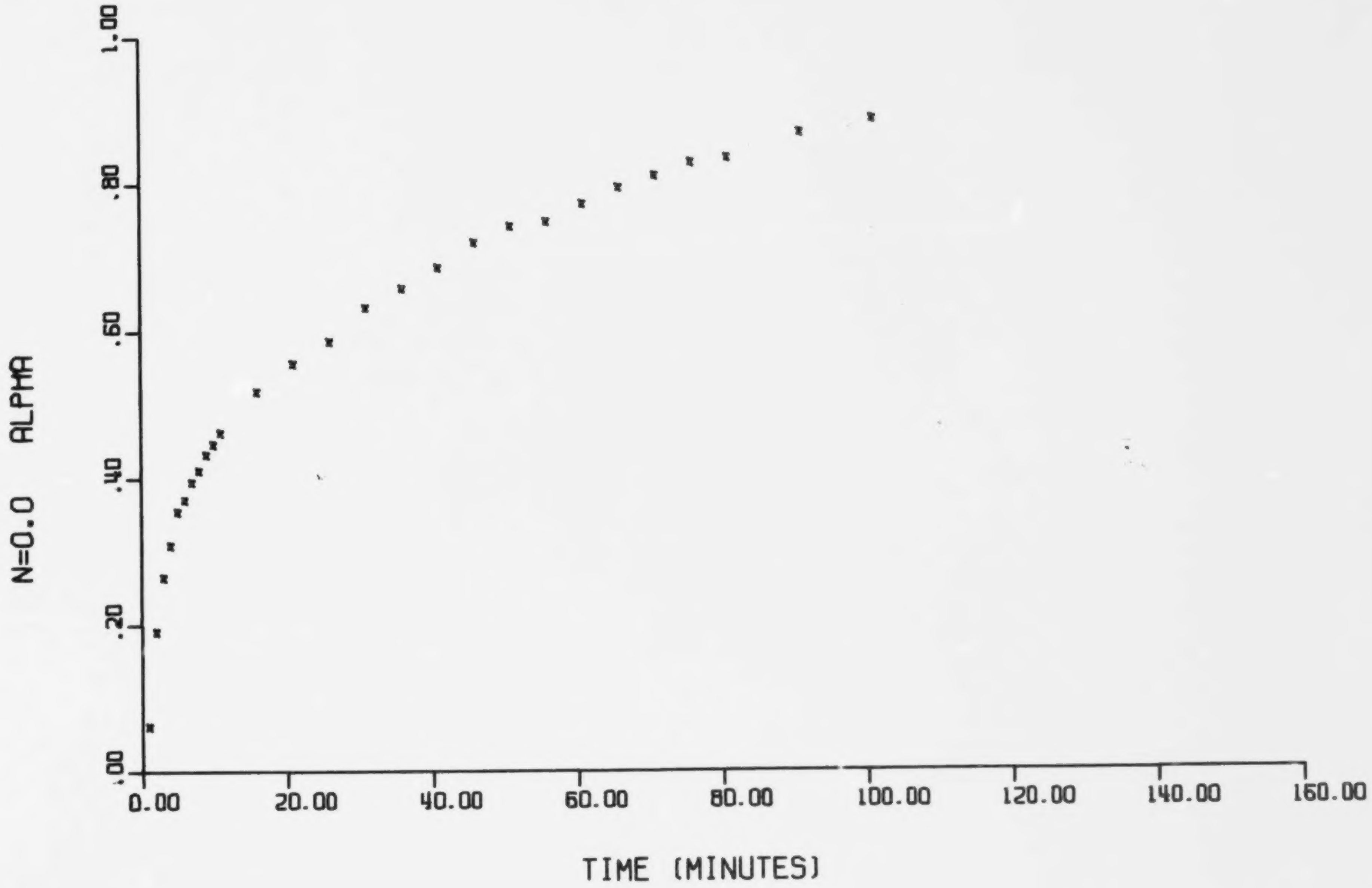
TRACOR

CR203 634-59-2
SO2 CONC = 0.122 TEMP = 336 DEG C



28 APR 69

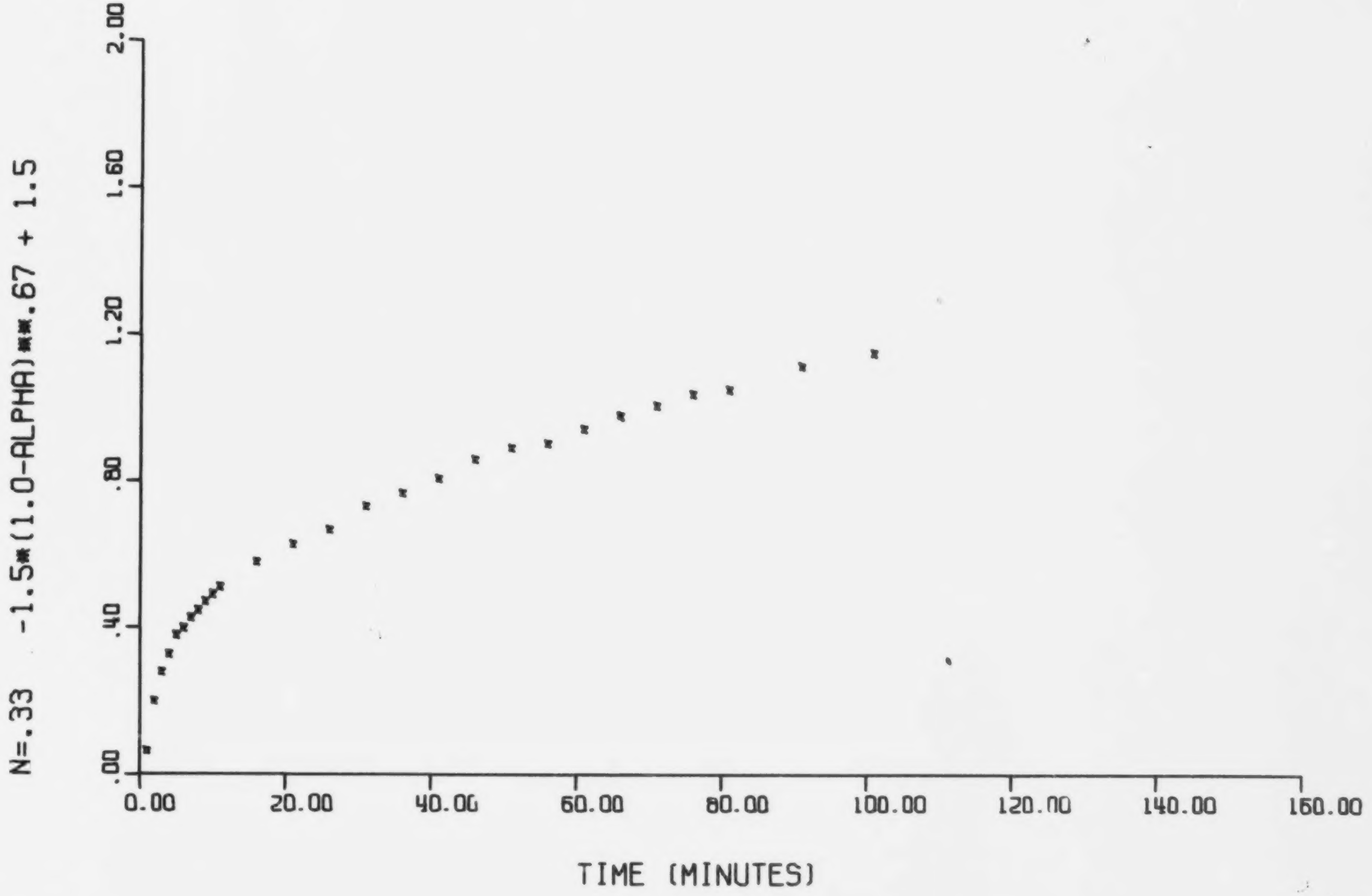
CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

TRACOR

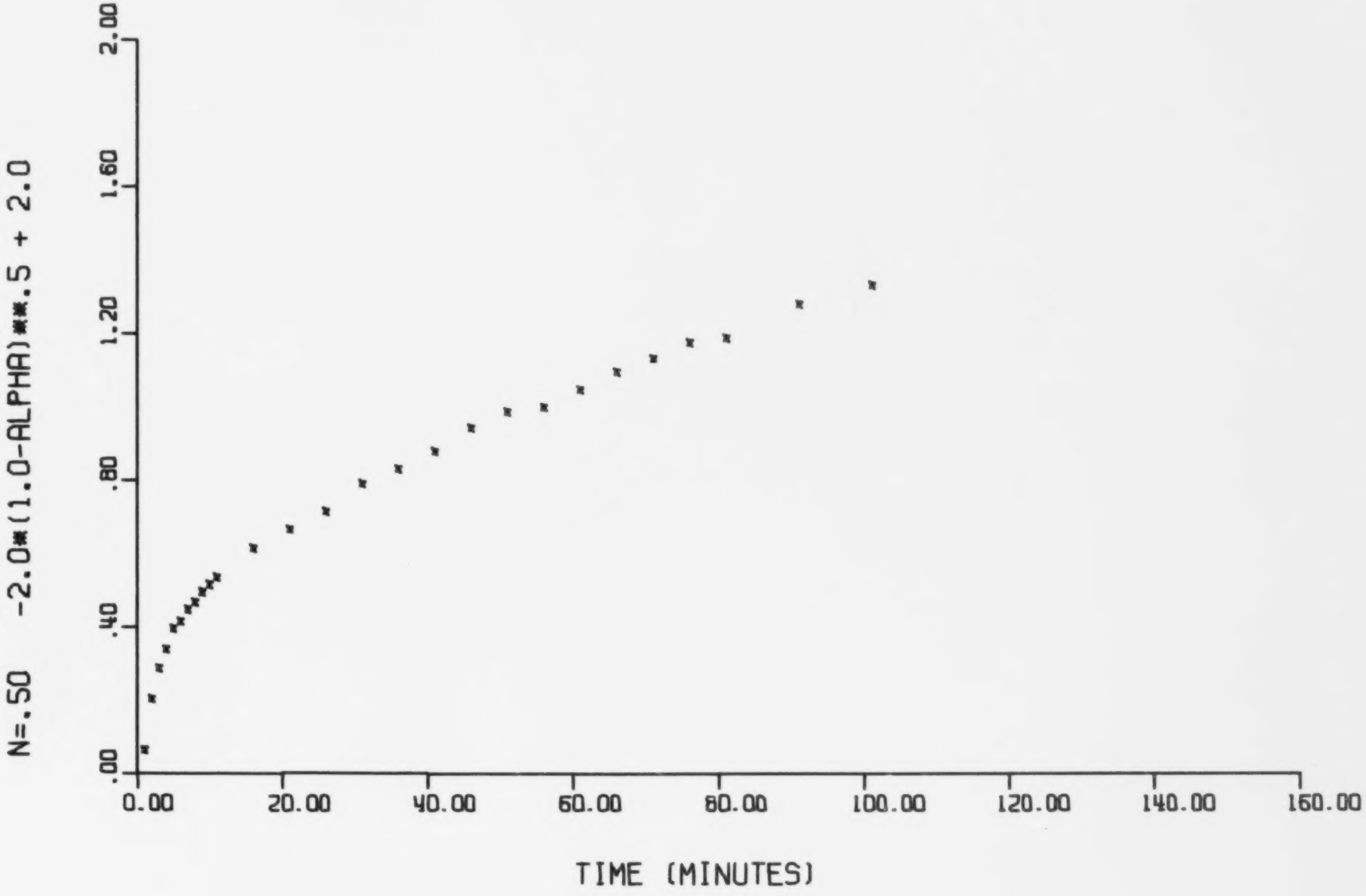
CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

TRACOR

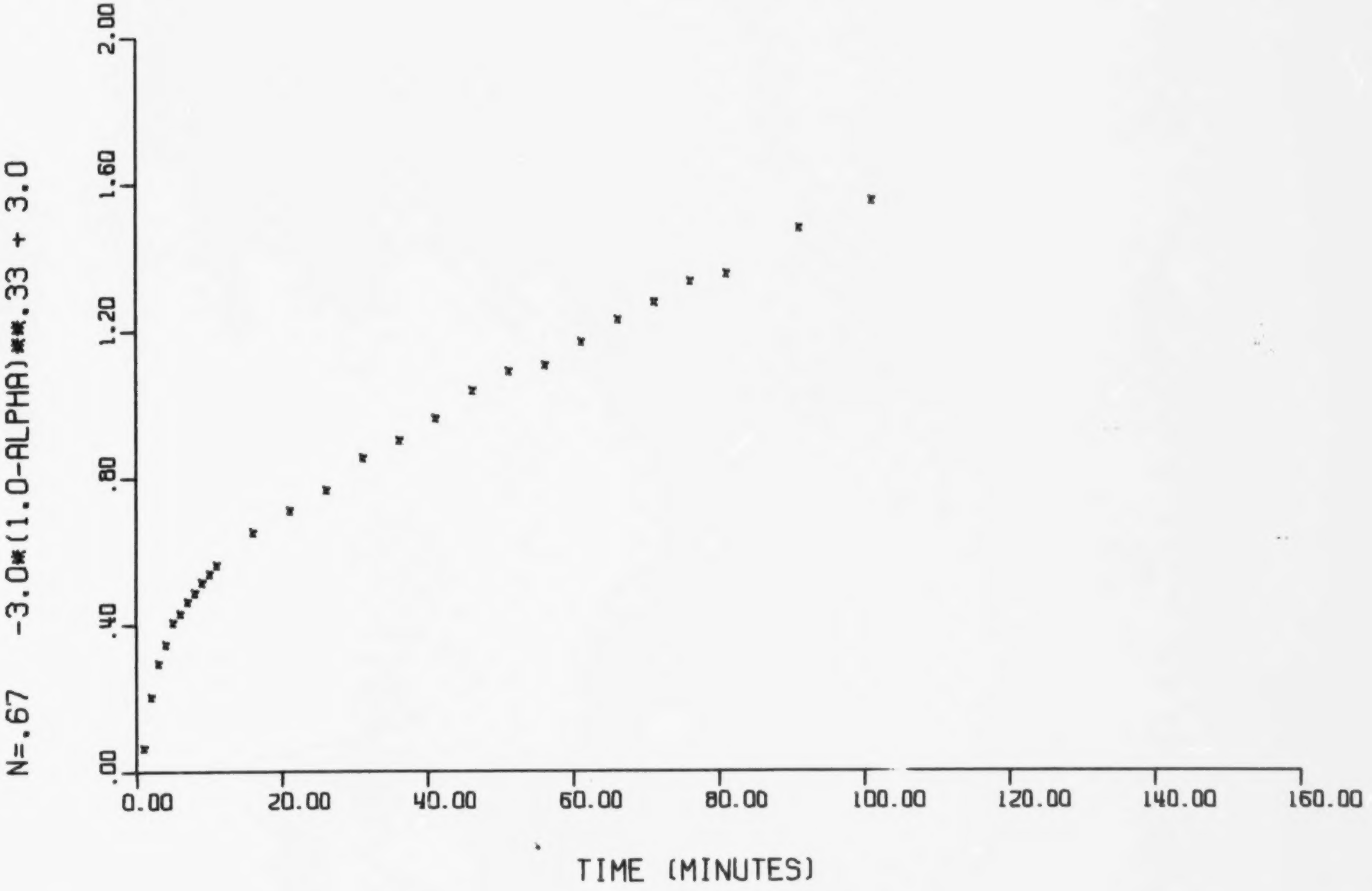
CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

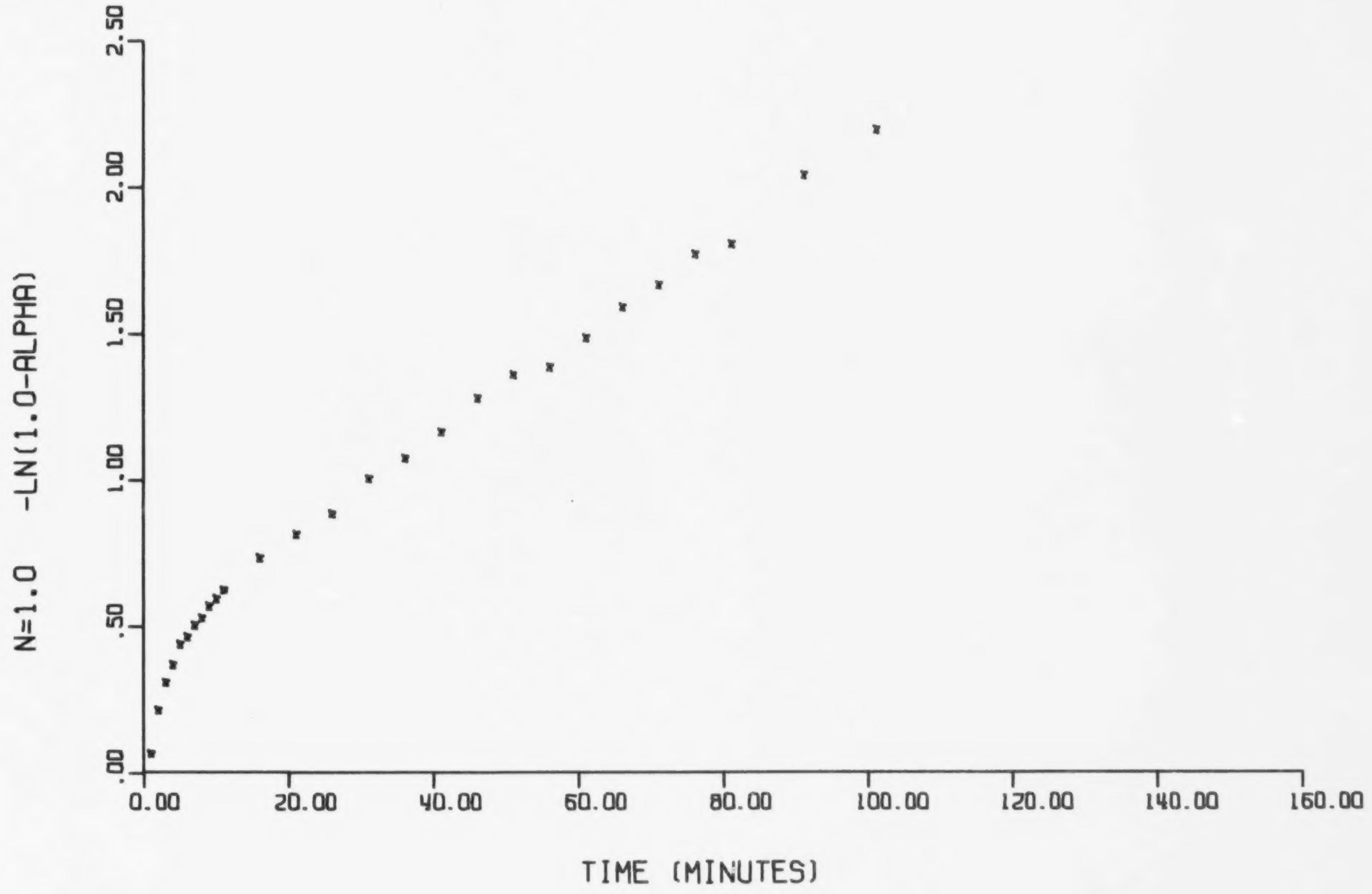
TRACOR

CR2O3 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



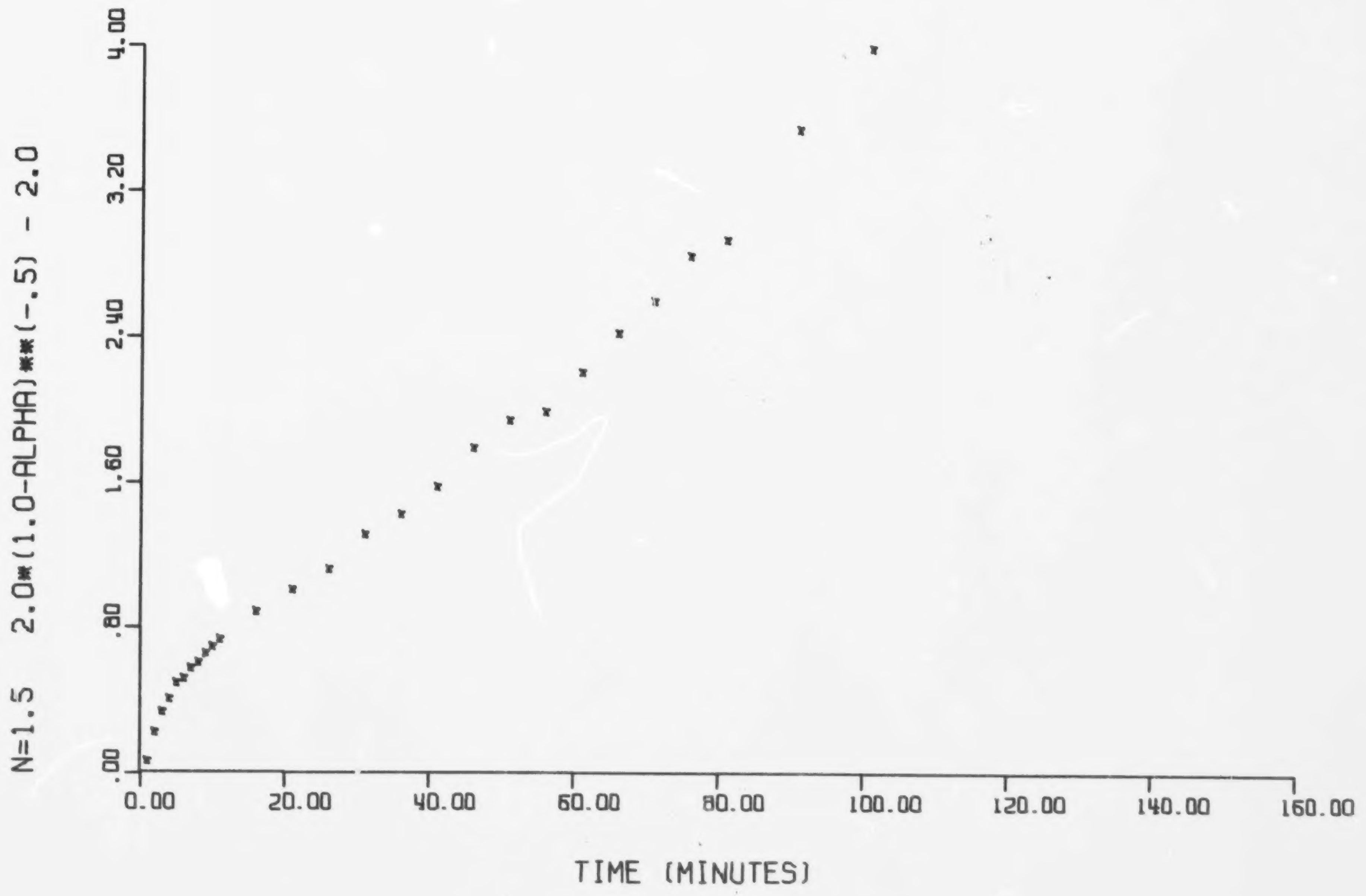
31 MAR 69

CR2O3 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

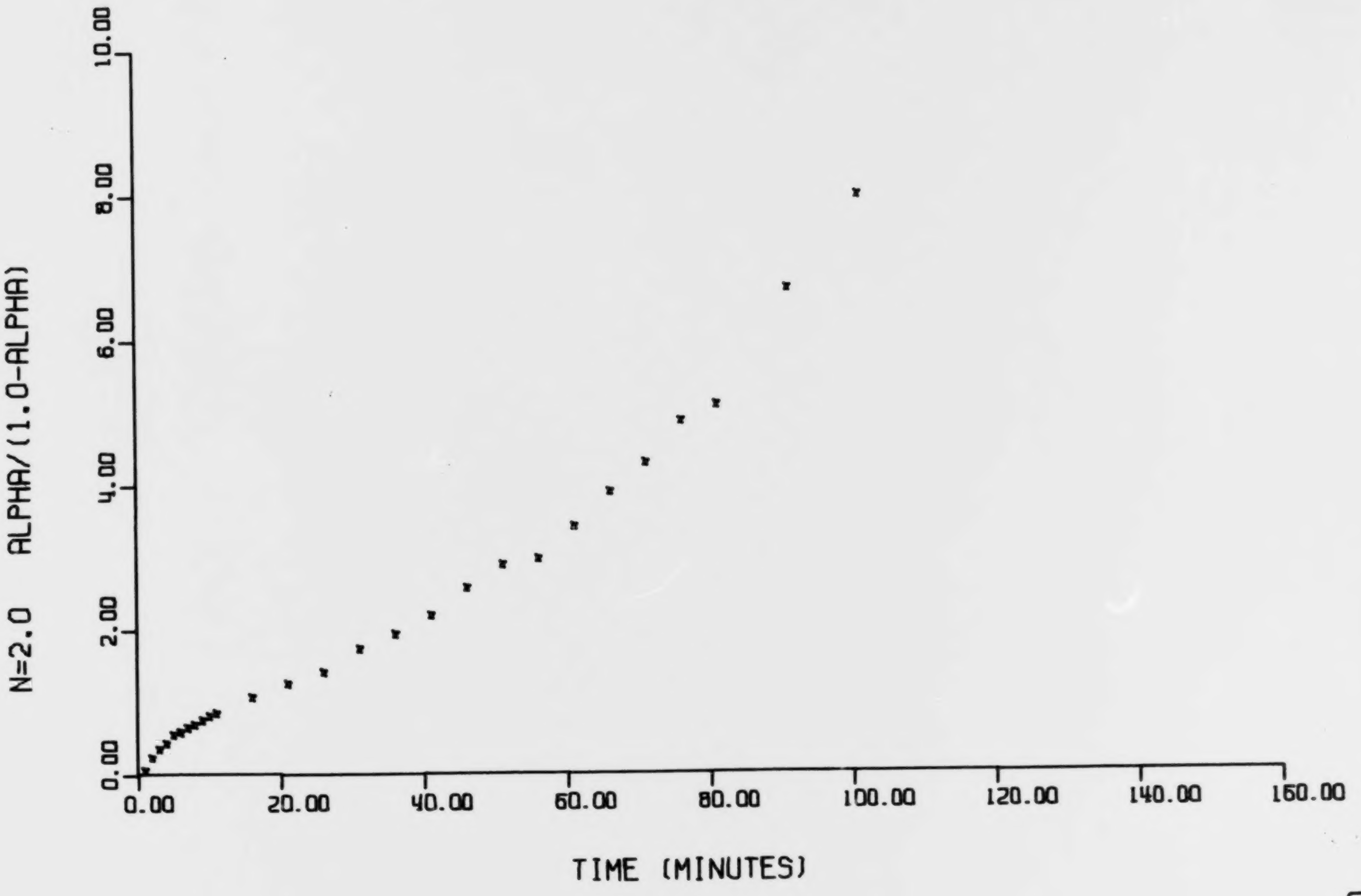
CR2O3 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

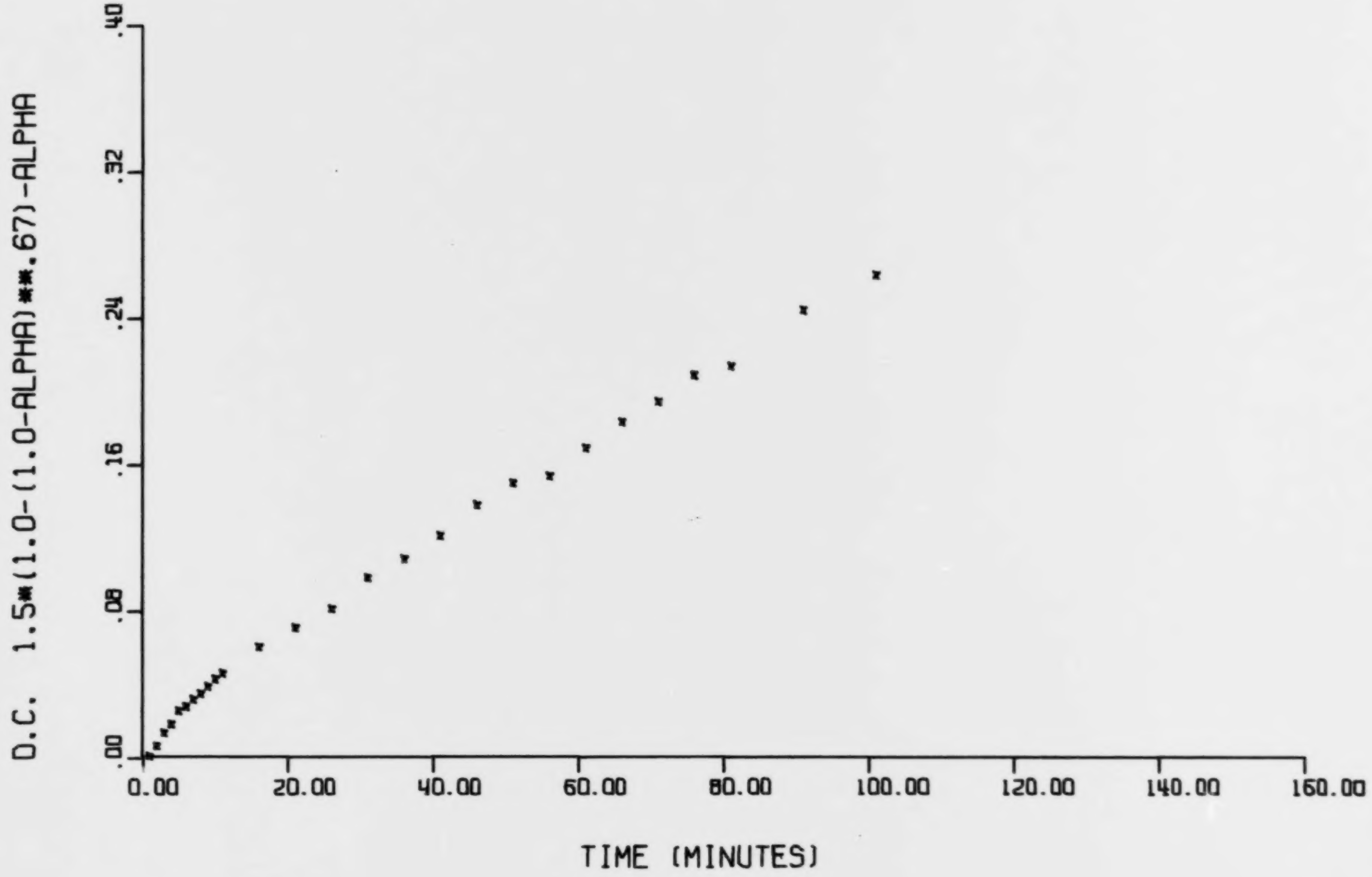
TRACOR

CR2O3 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

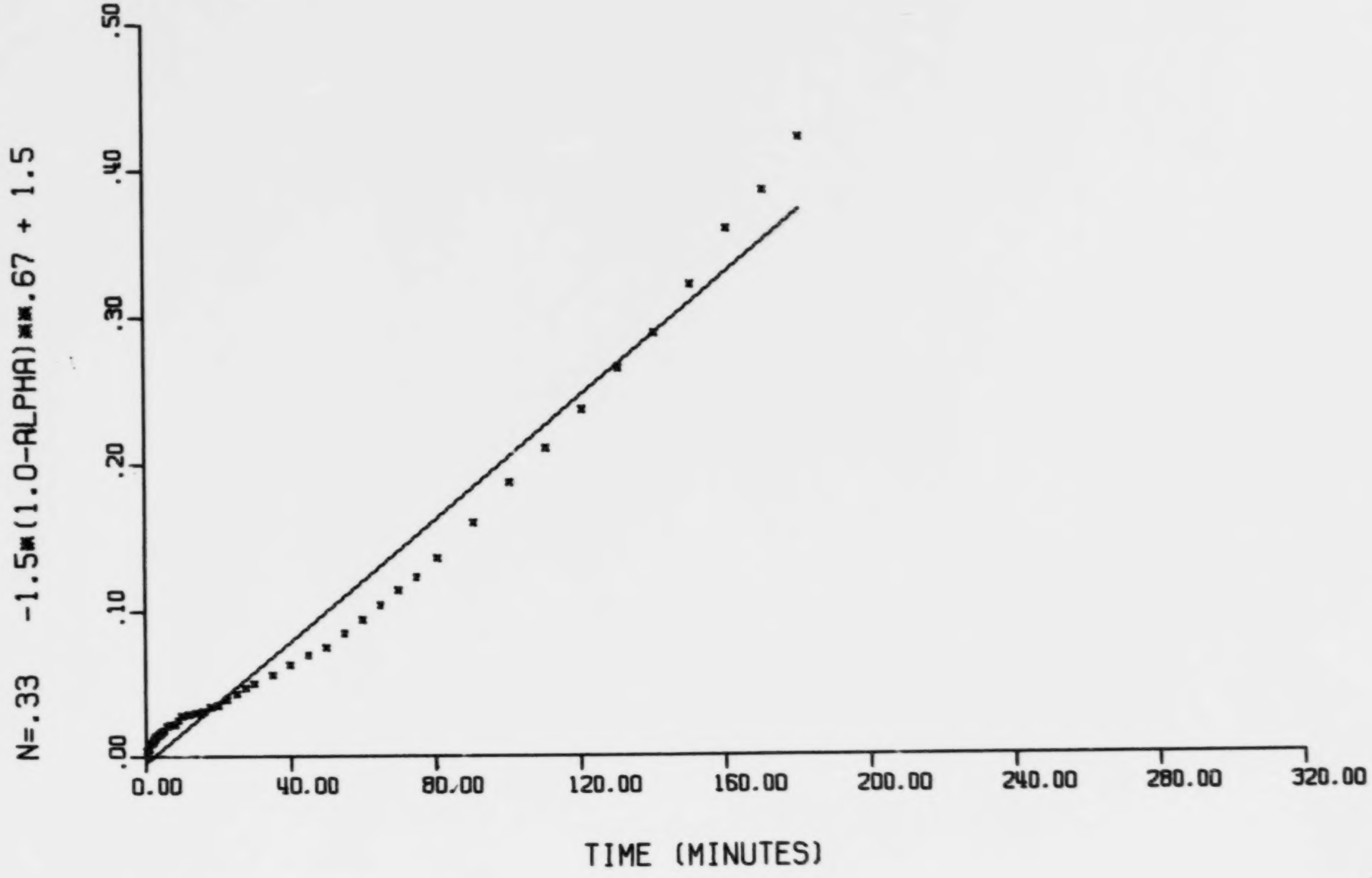
CR203 634-59-2
ISO-TGA-2 TEMP = 335 DEG C.



31 MAR 69

TRACOR

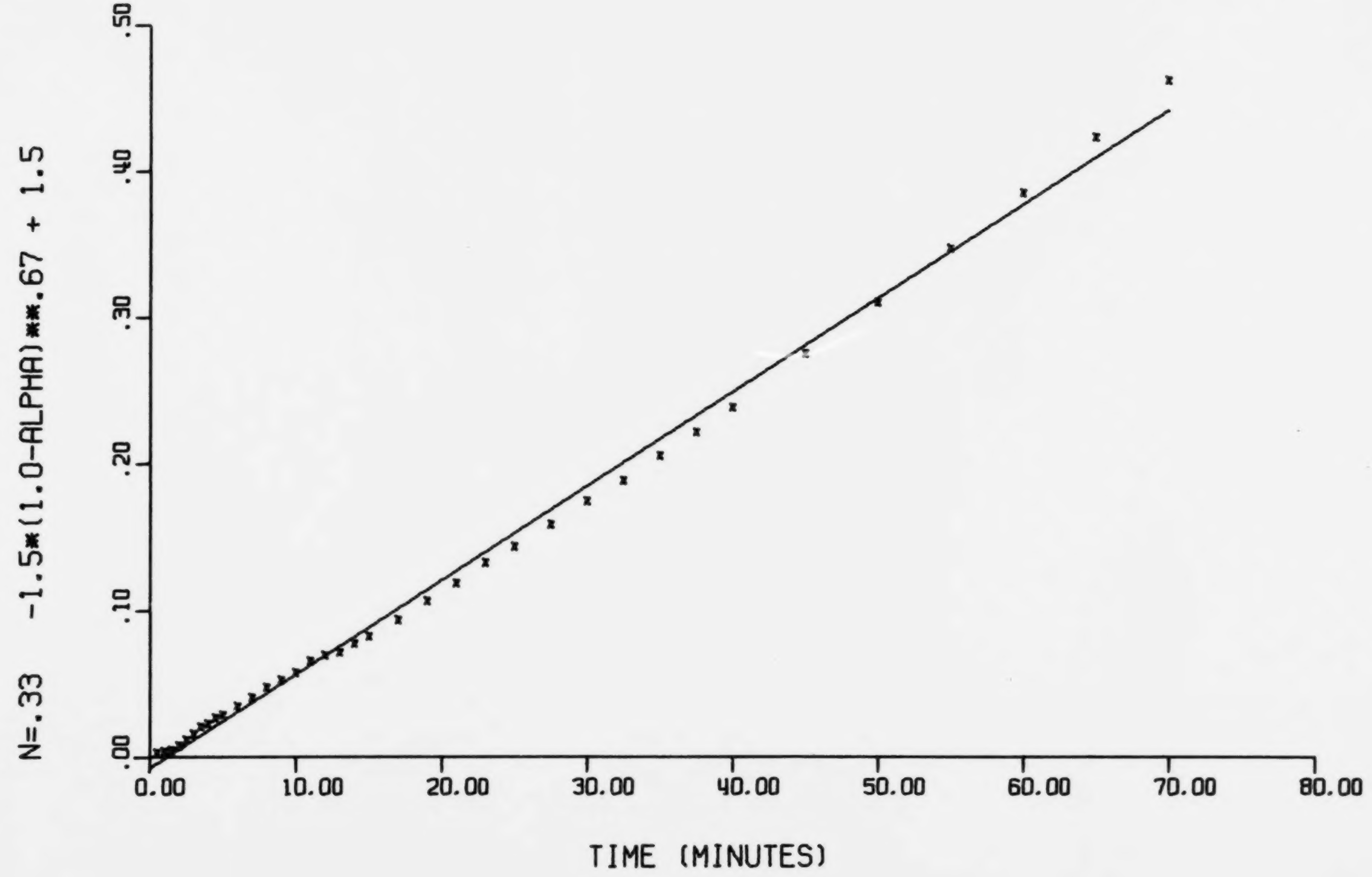
CUO 634-47-1
ISO TGA 5 TEMP = 325 DEG C



17 JUN 69

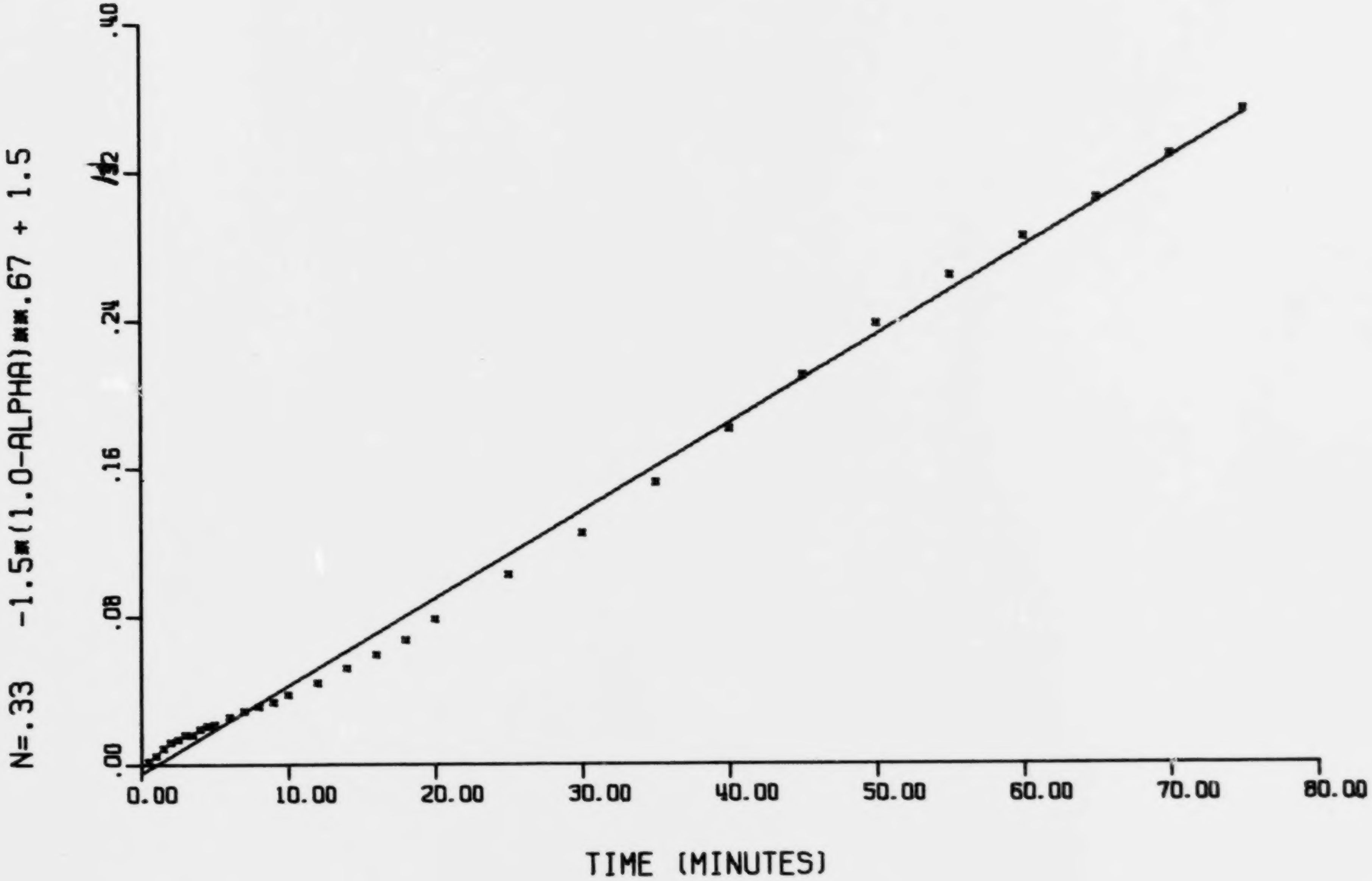
TRACOR

CUO 634-47-1
ISO TGA 4 TEMP = 352 DEG C



18 APR 69

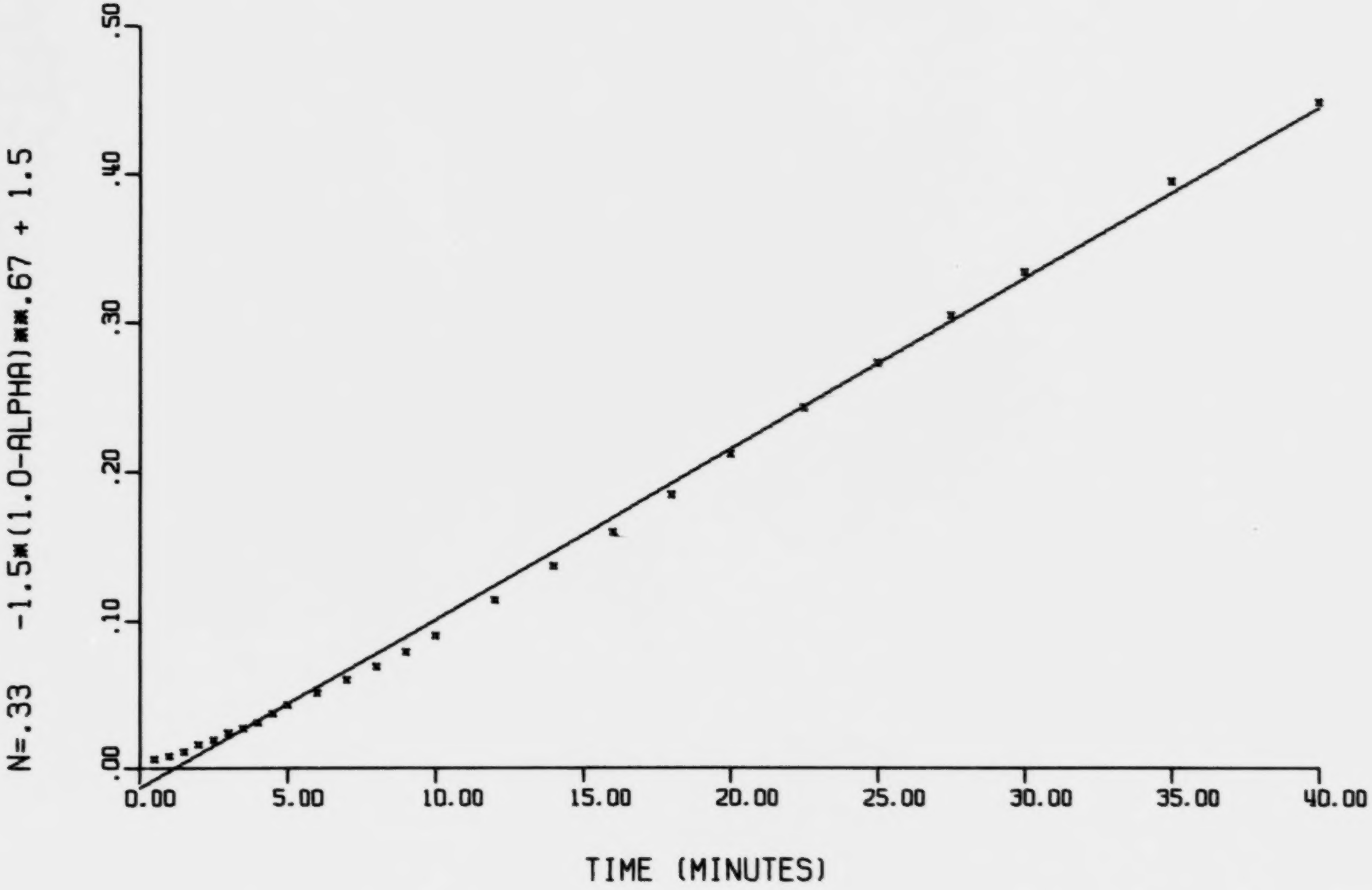
TRACOR


CUO 634-47-1
REGEN TGA 1-1 TEMP = 355 DEG C

21 MAY 69

TRACOR

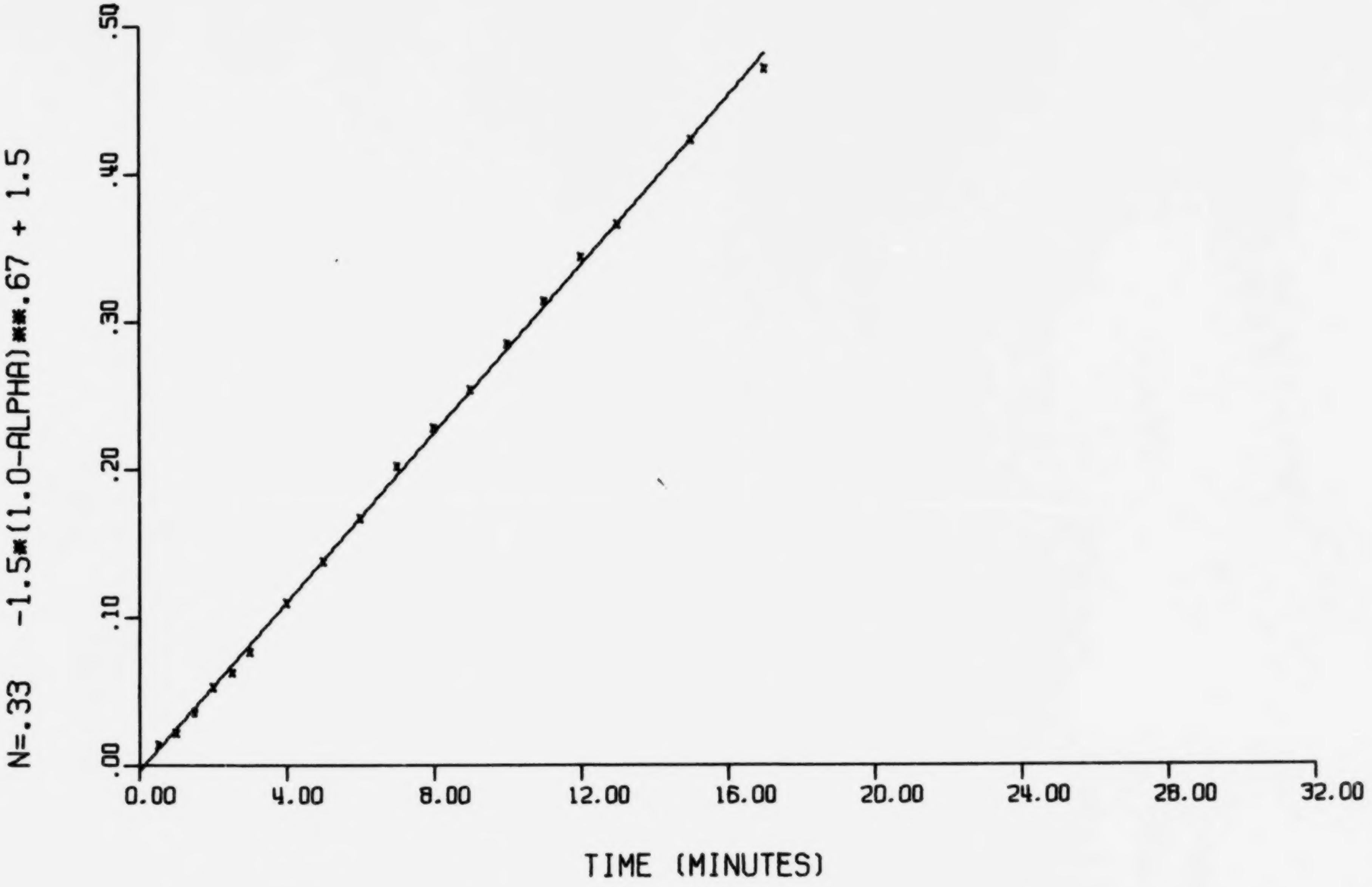
CUO 634-47-1
ISO-TGA-6 TEMP = 376 DEG C



17 JUN 69

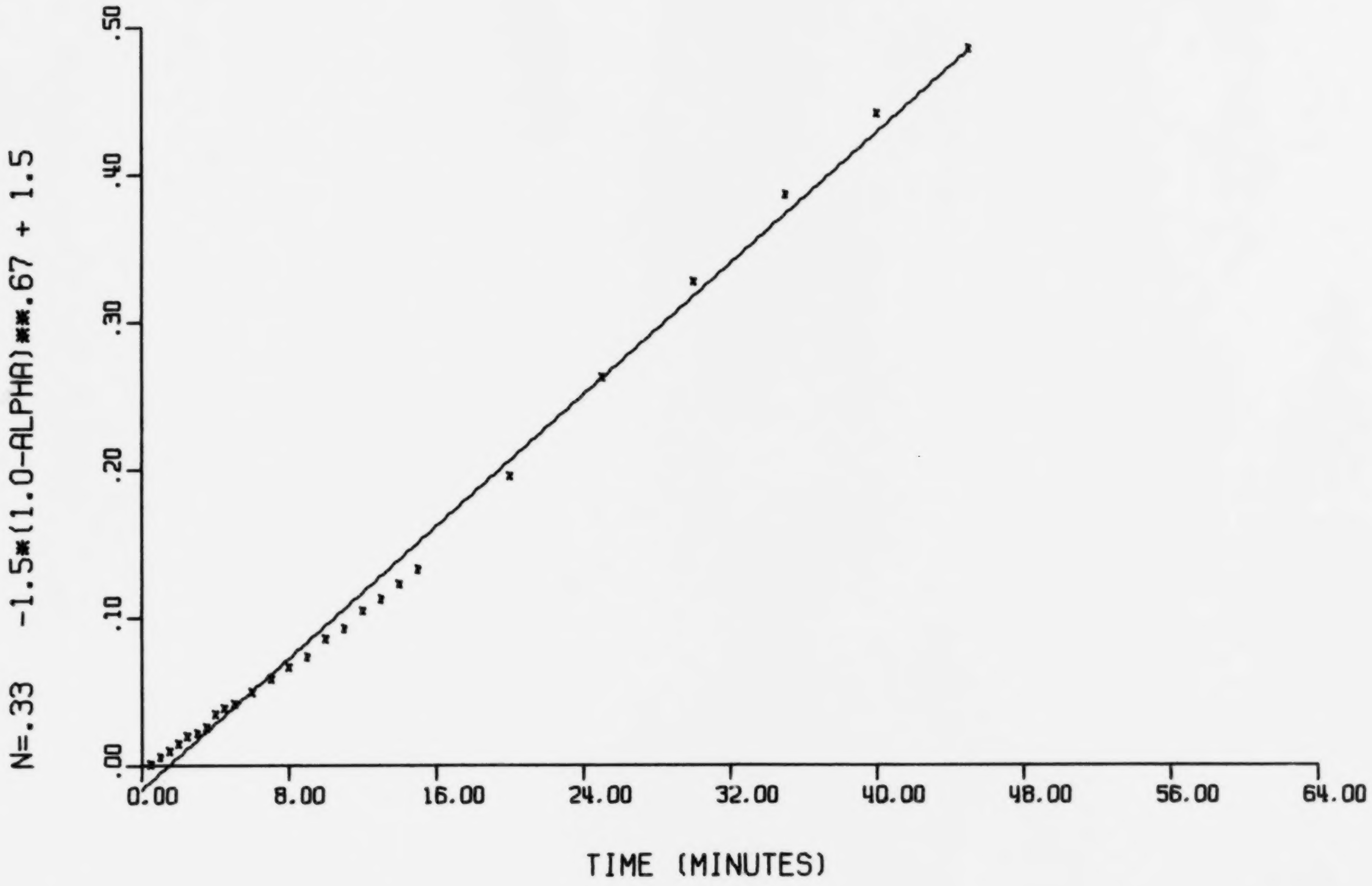
TRACOR

CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



18 APR 69

CUO 634-47-1
SO2 CONC = 0.122 TEMP = 404 DEG C

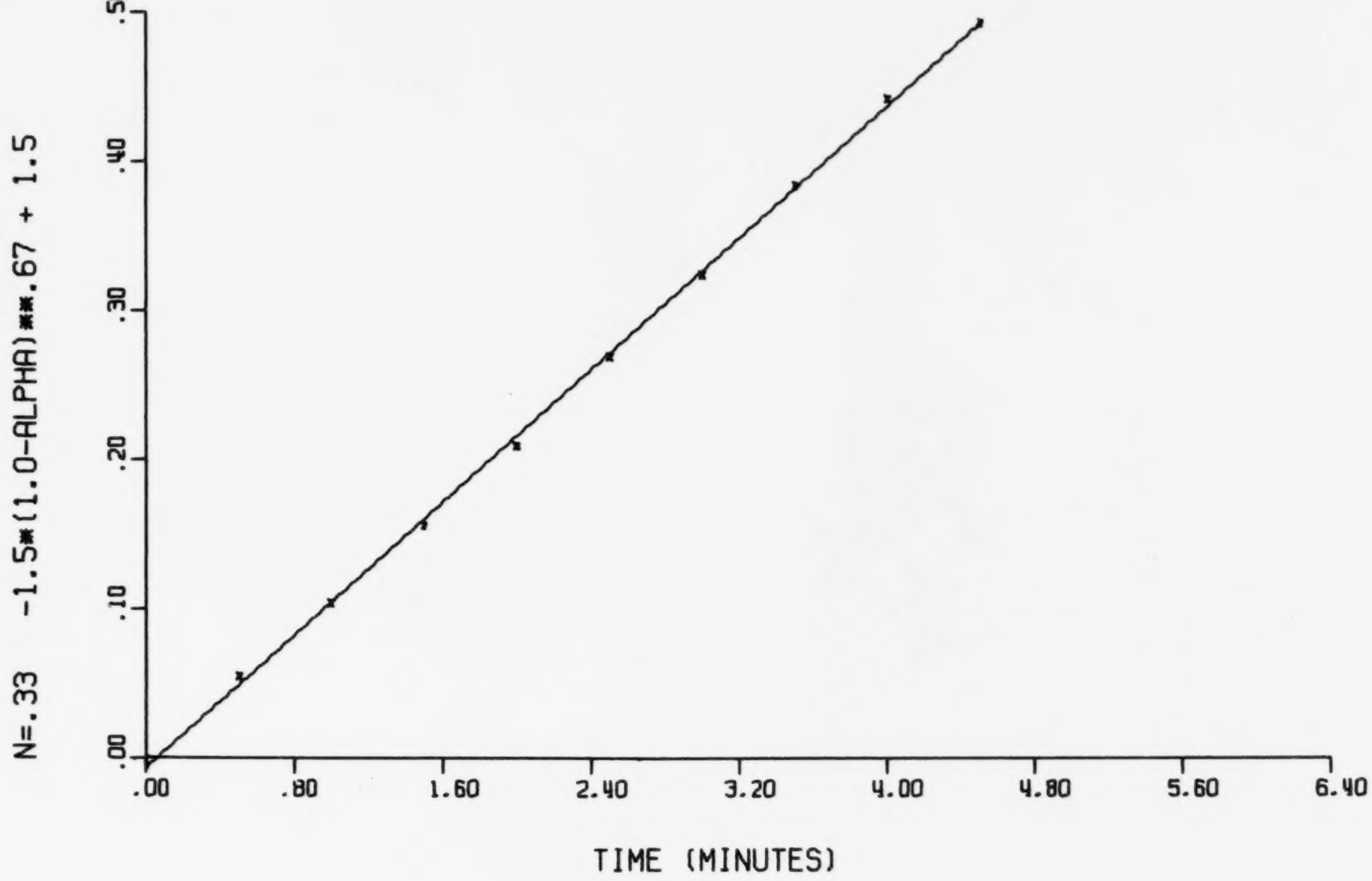


18 APR 69

TRACOR

CUO 634-47-1   ISO TGA-2

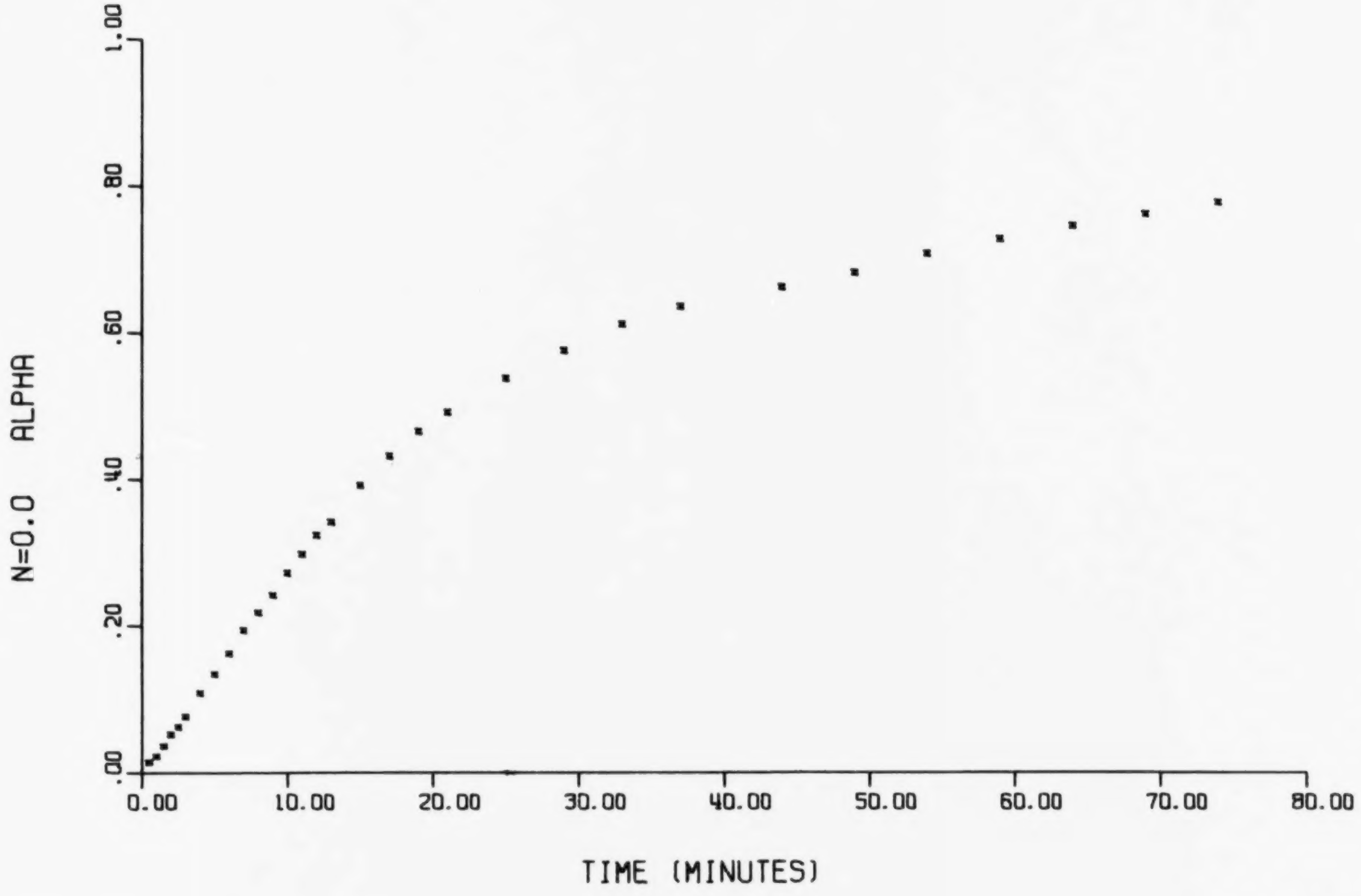
482 DEG C



18 APR 69

TRACOR

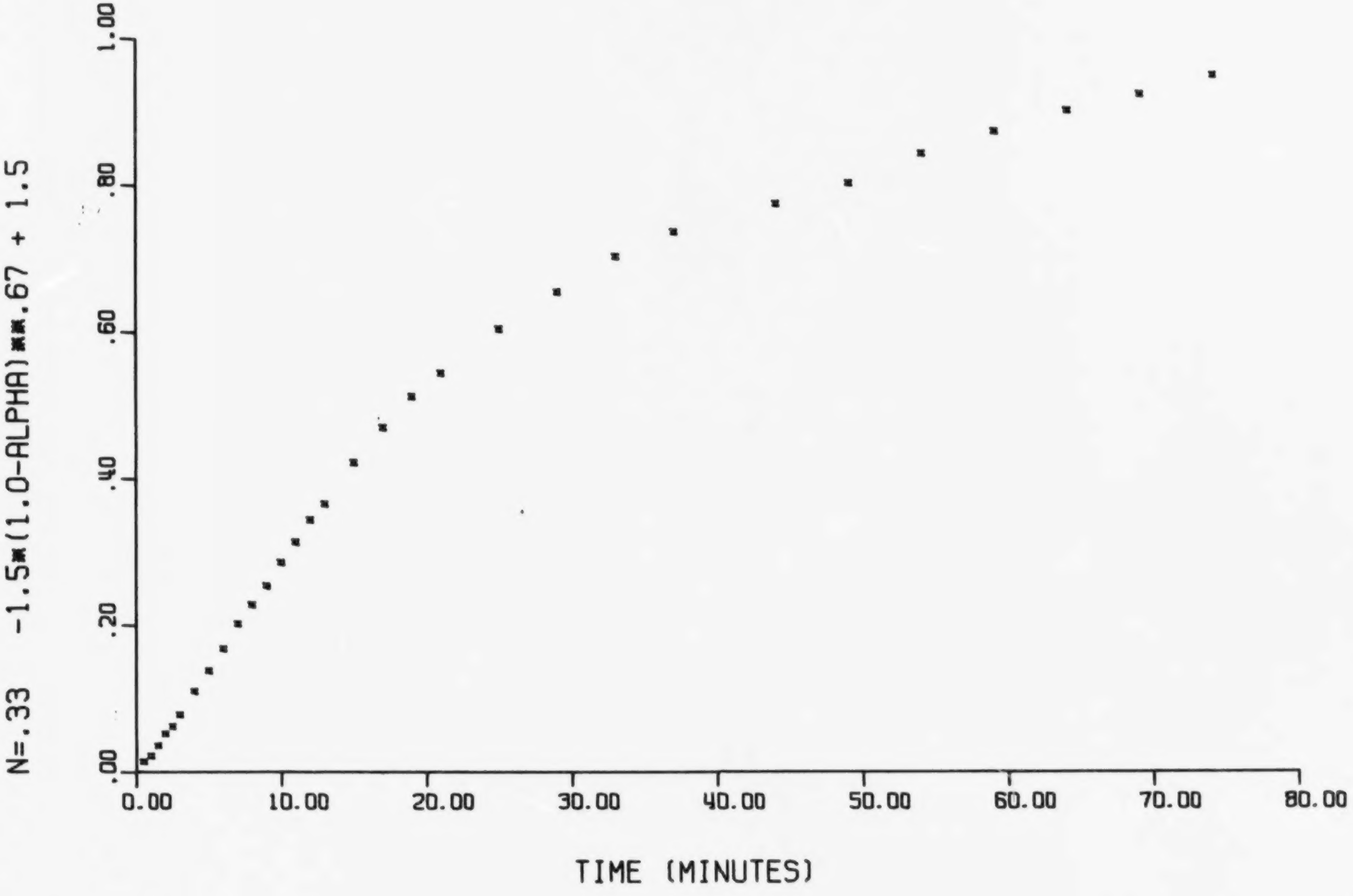
CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



24 MAR 69

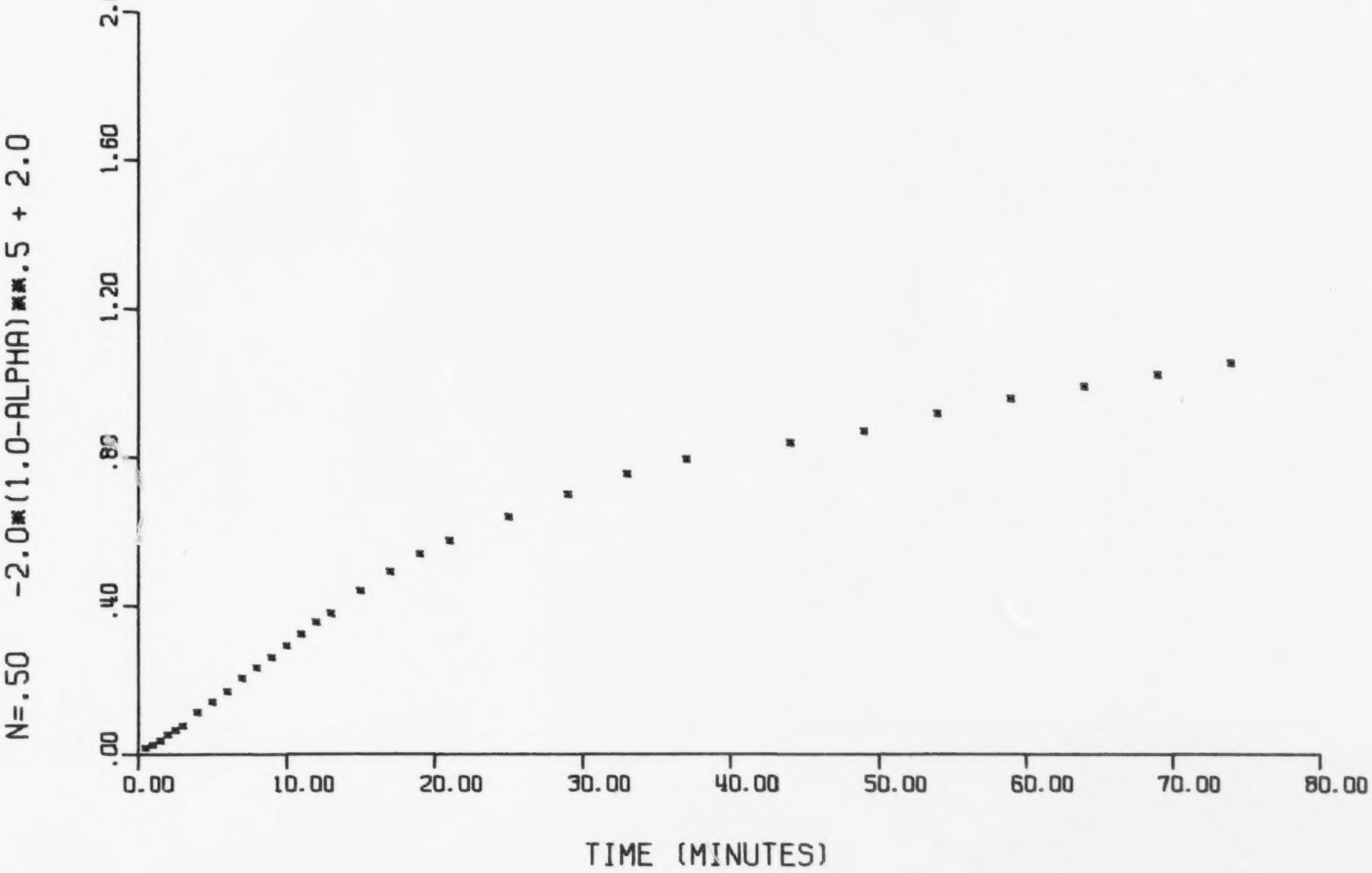
TRACOR

CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



24 MAR 69

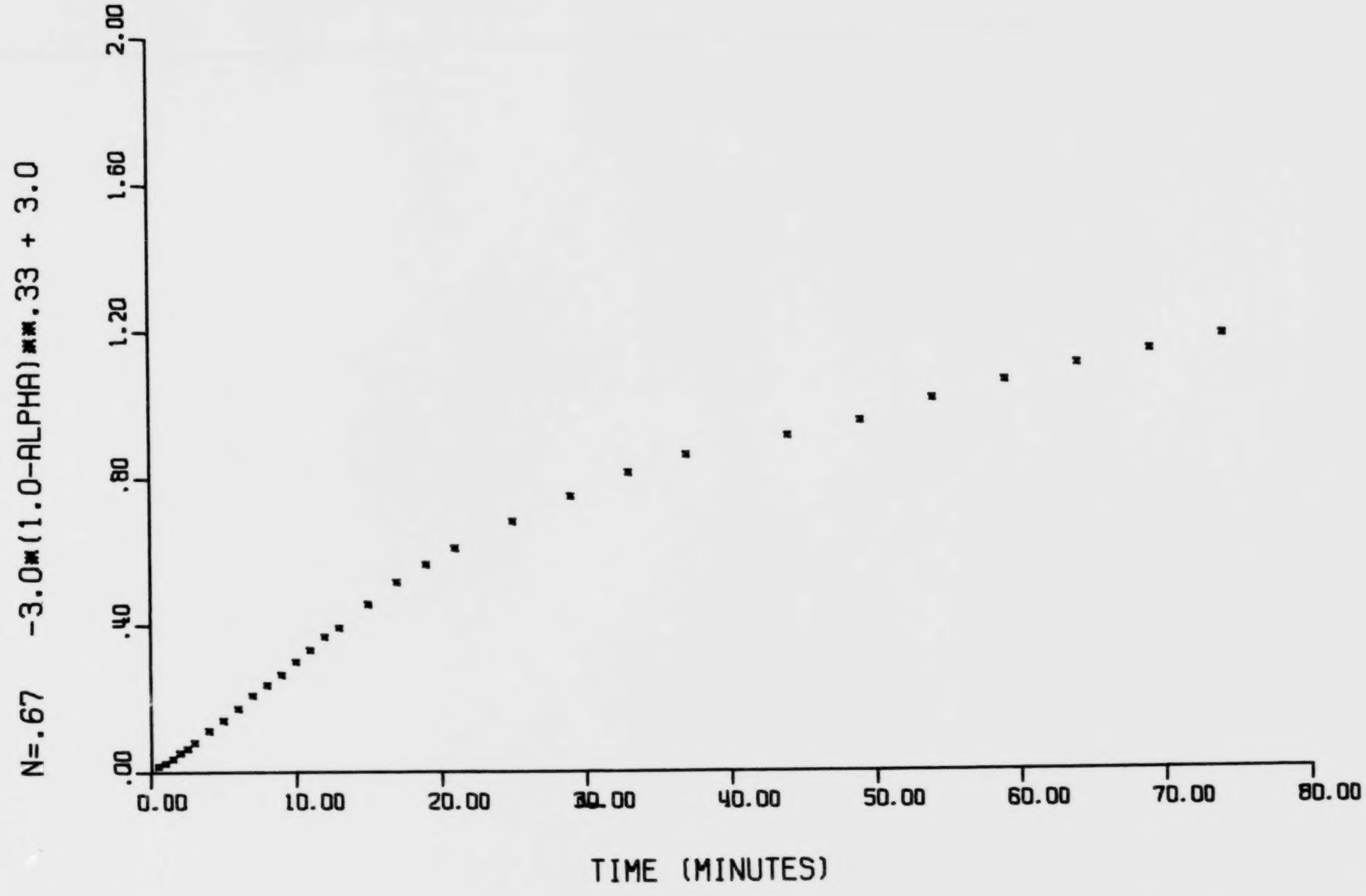
CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



24 MAR 69

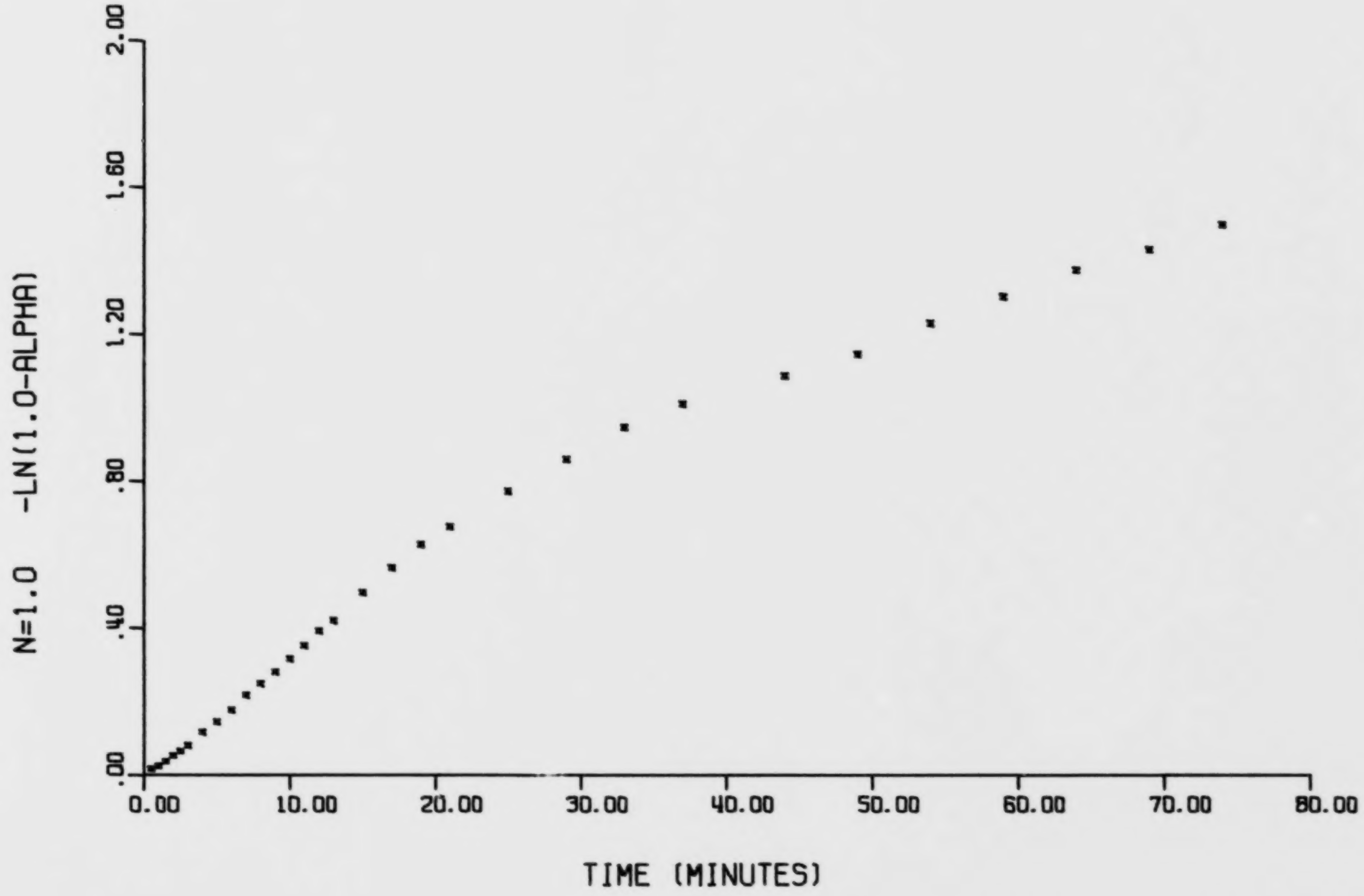
TRACOR

CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C



24 MAR 69

CUO 634-47-1
ISO-TGA-1   TEMP = 404 DEG C

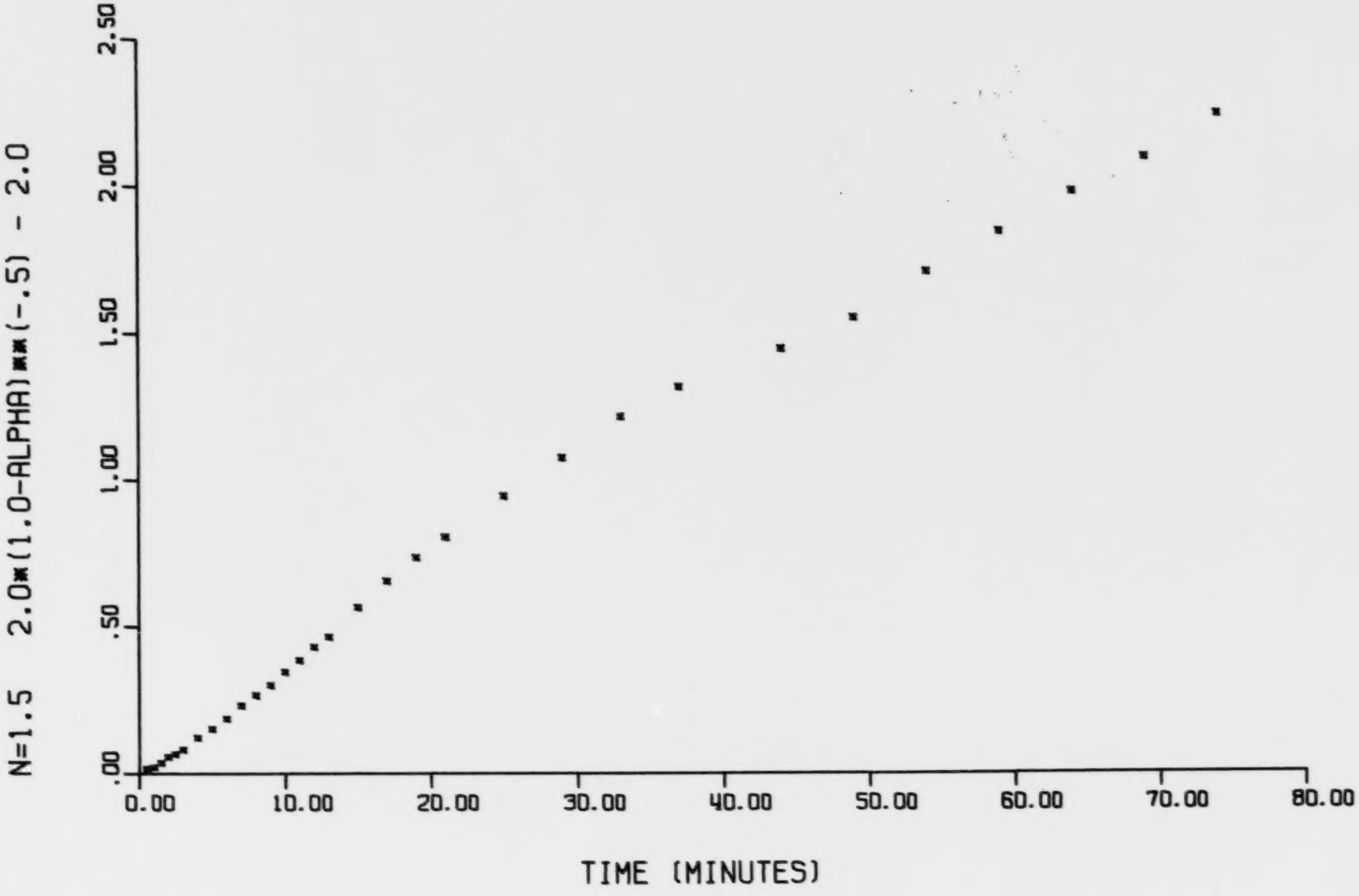


24 MAR 69

TRACOR

CUO 634-47-1

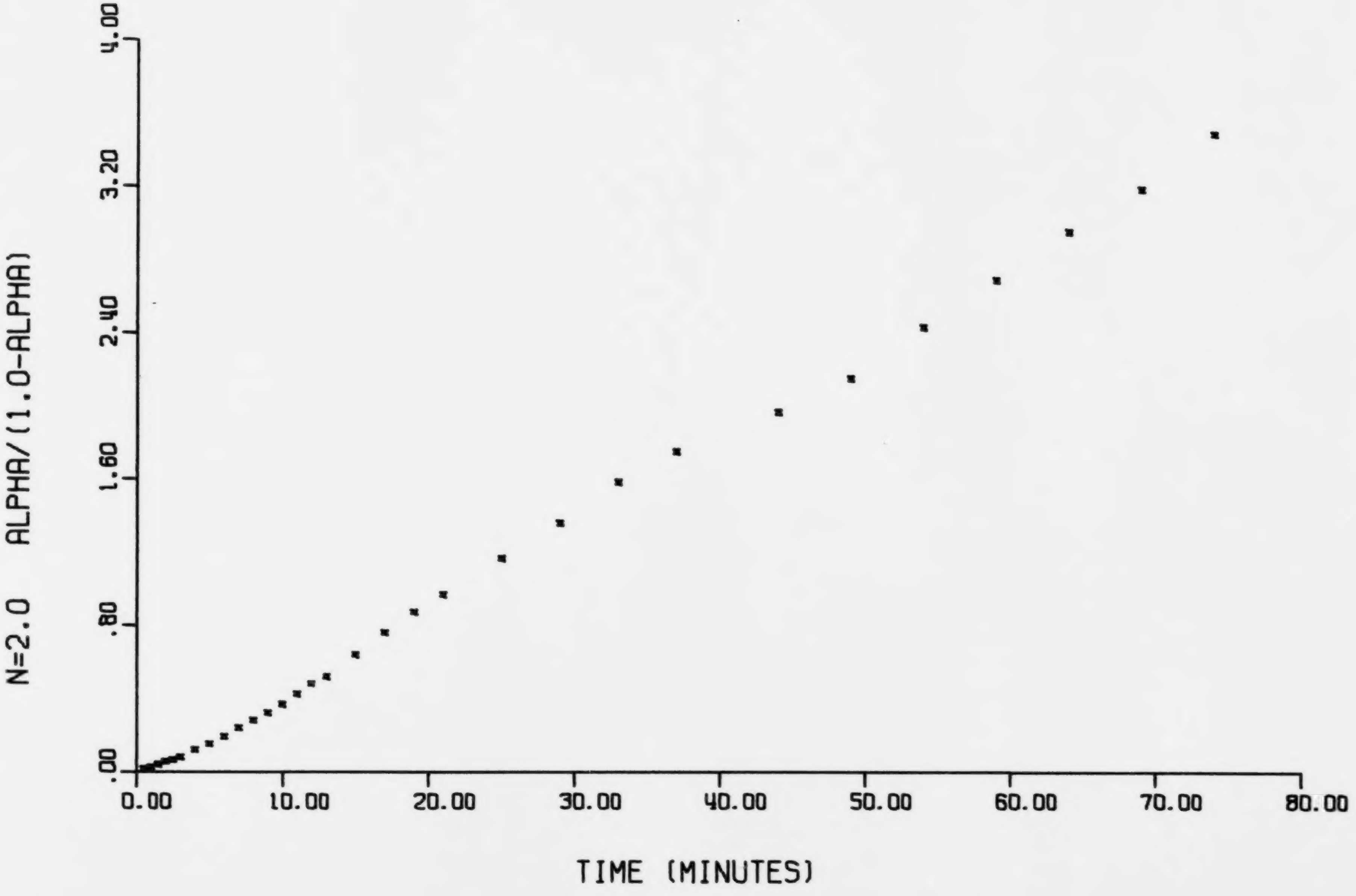
ISO-TGA-1 TEMP = 404 DEG C



24 MAR 69

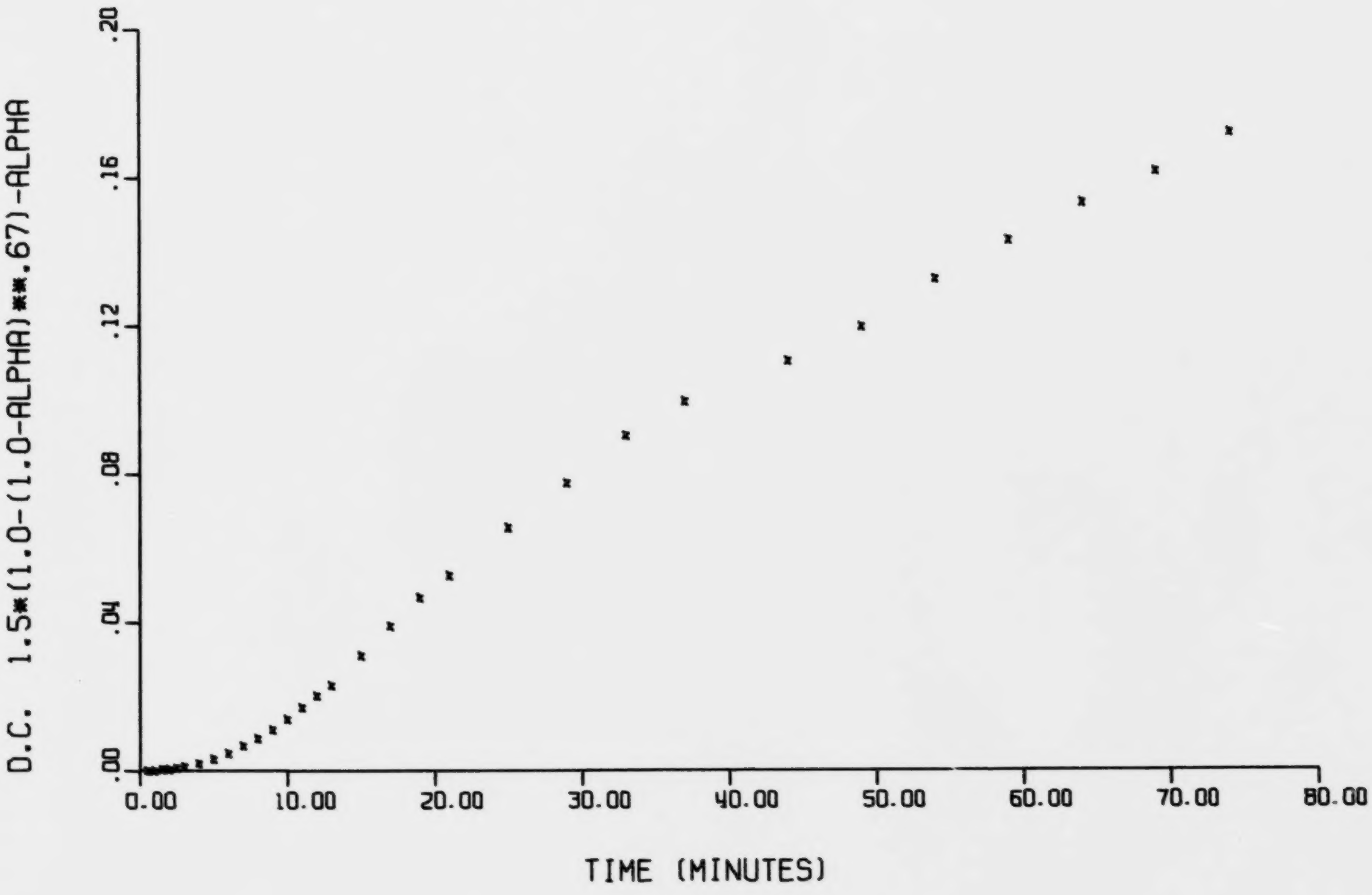
TRACOR

CUO 634-47-1
ISO-TGA-1 TEMP = 404 DEG C



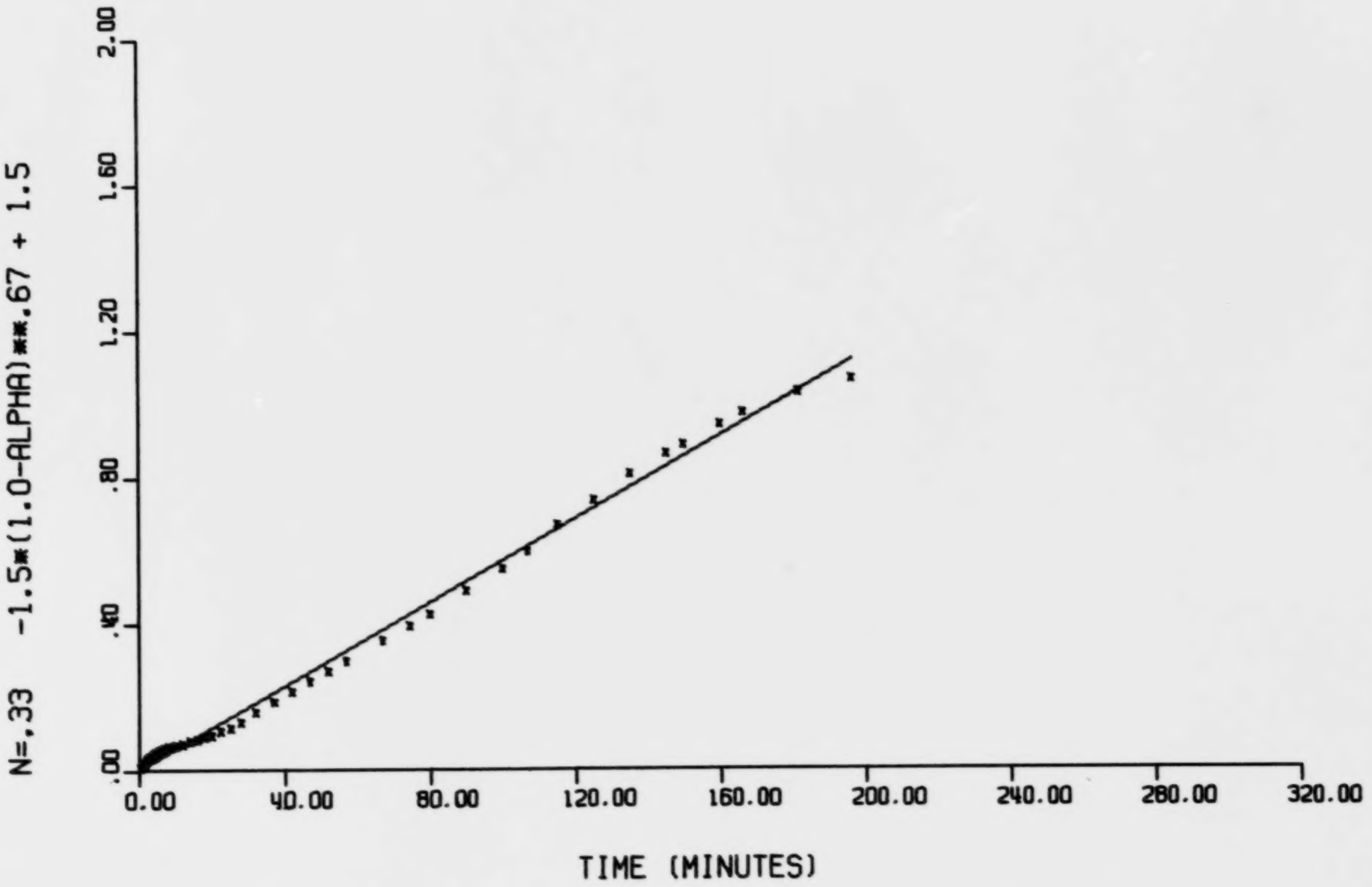
24 MAR 69

CUO 634-47-1
ISO-TGA-1 TEMP = 404 DEG C



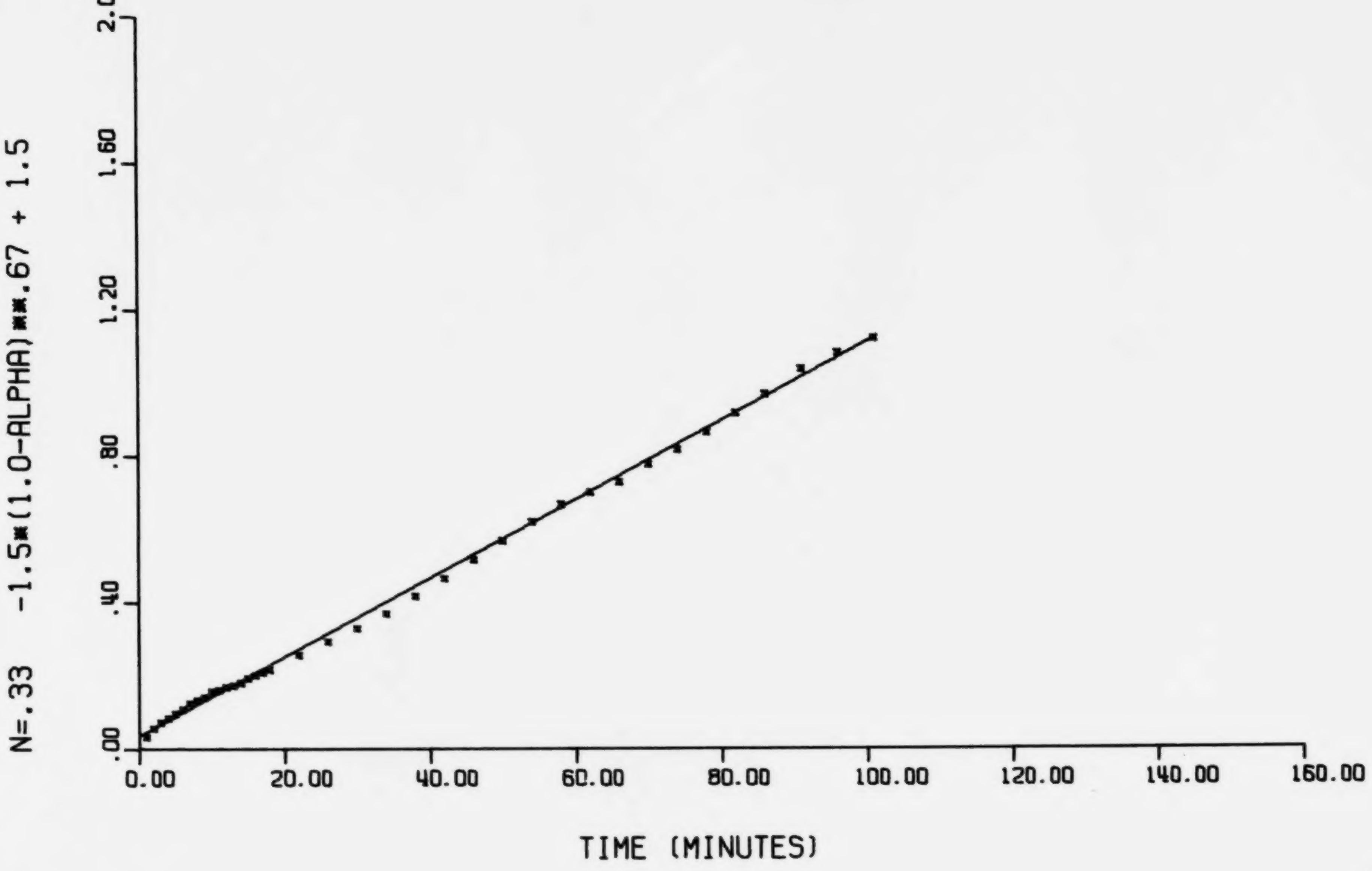
25 MAR 69

FE203 634-45-1
ISO-TGA 4 TEMP = 342 DEG C



4 JUN 69

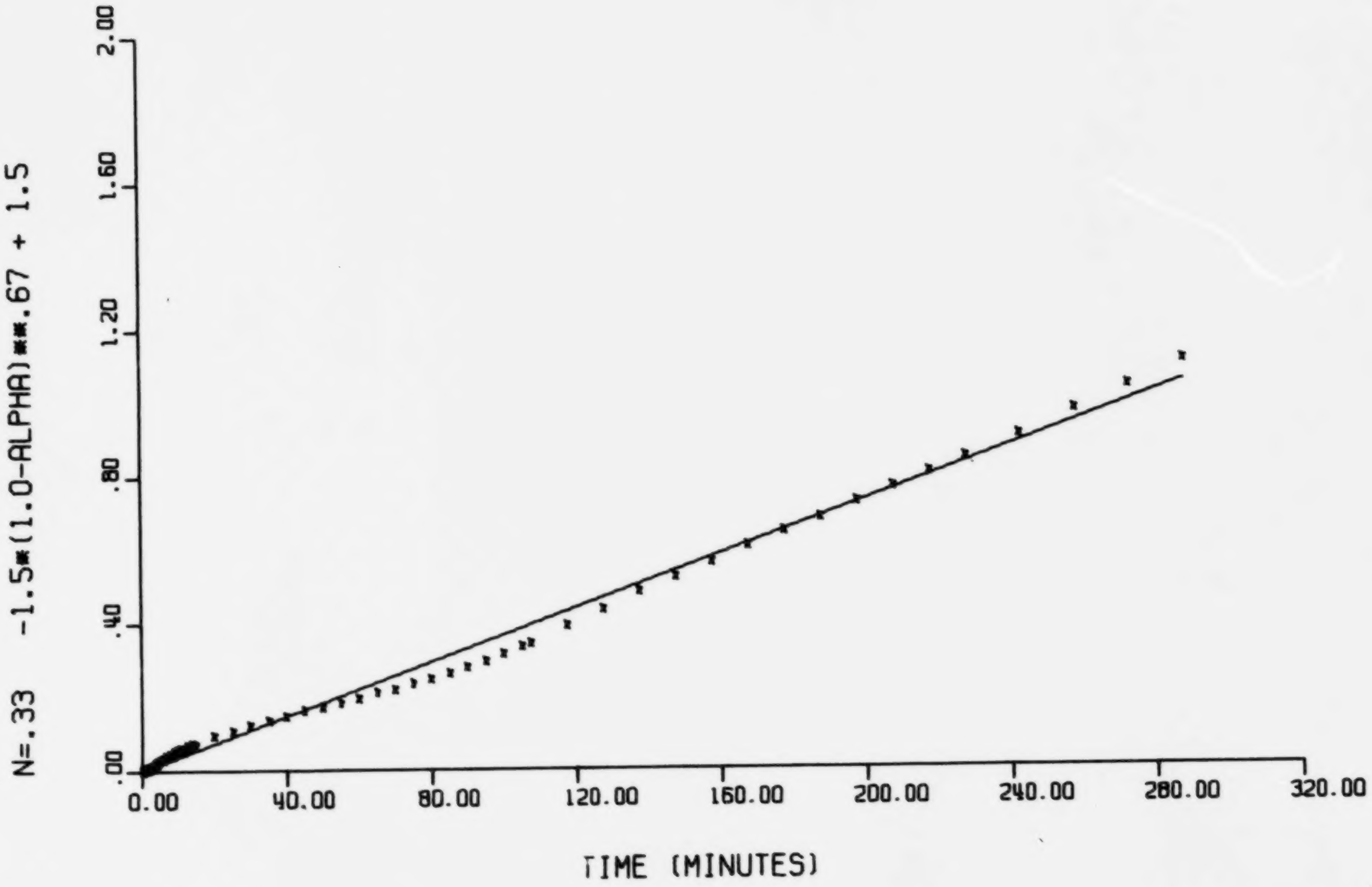
FE2O3 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



14 APR 69

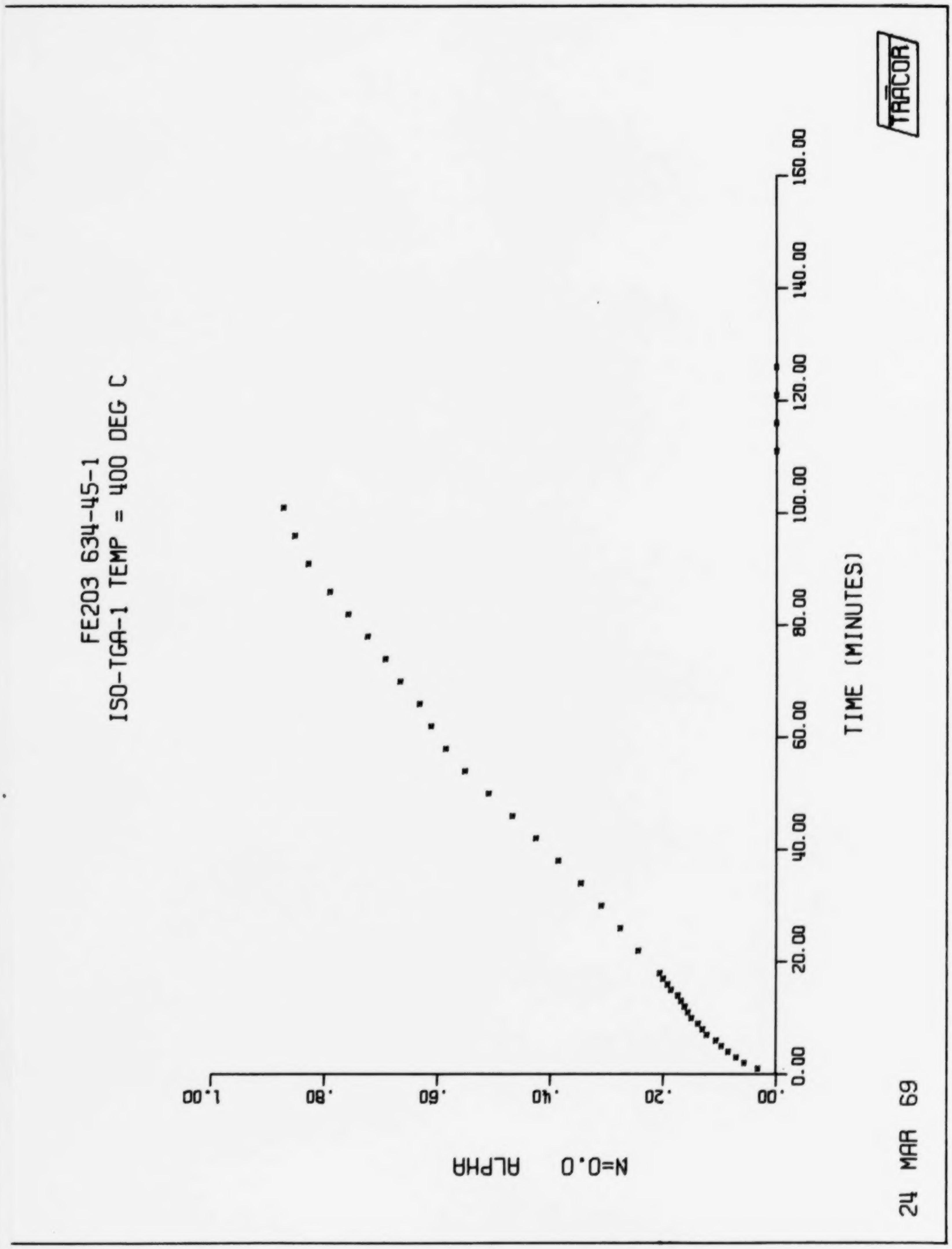
TRACOR

FE203 634-45-1
SO2 CONC = 0.120 TEMP = 400 DEG C

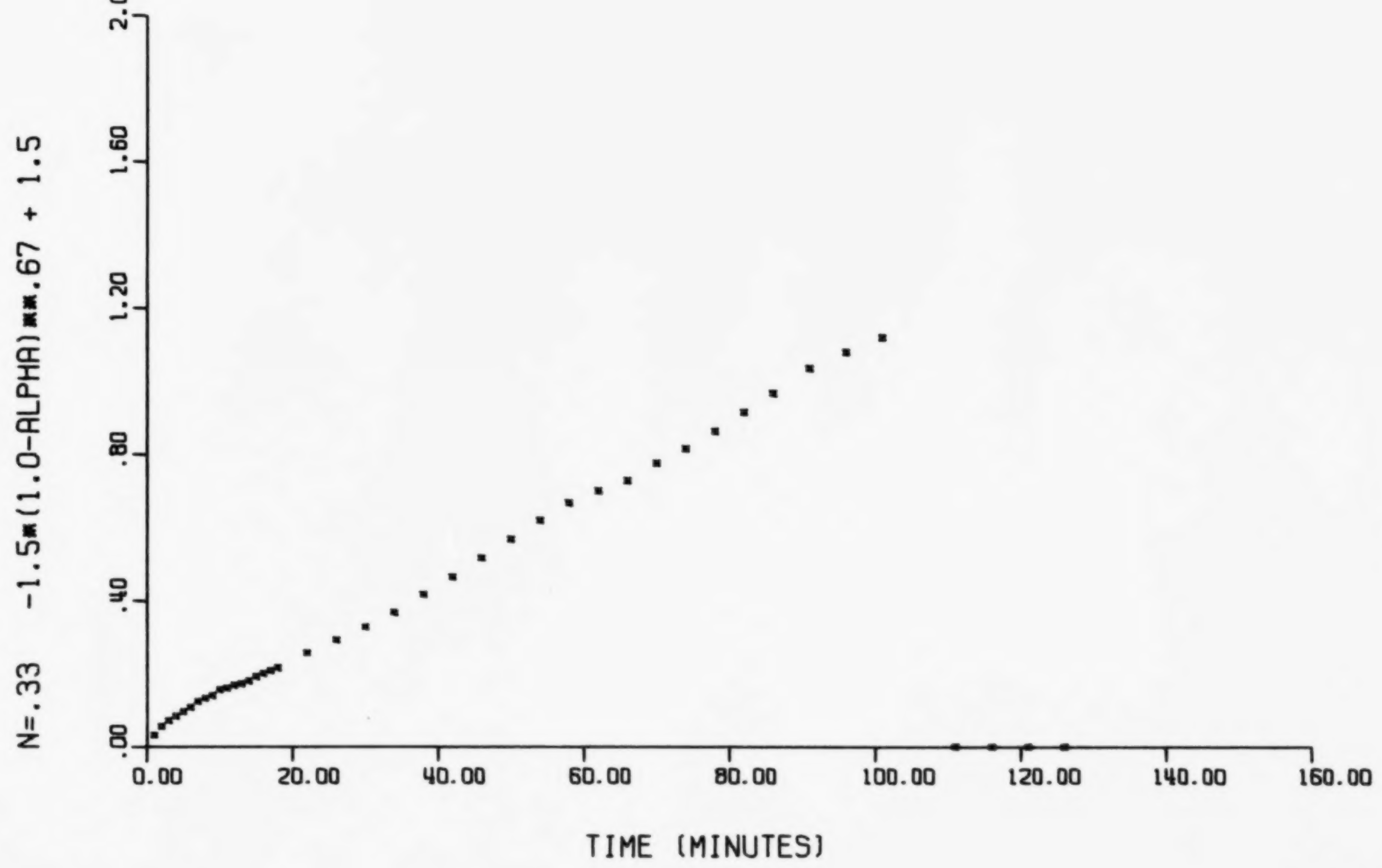


15 APR 69

TRACOR

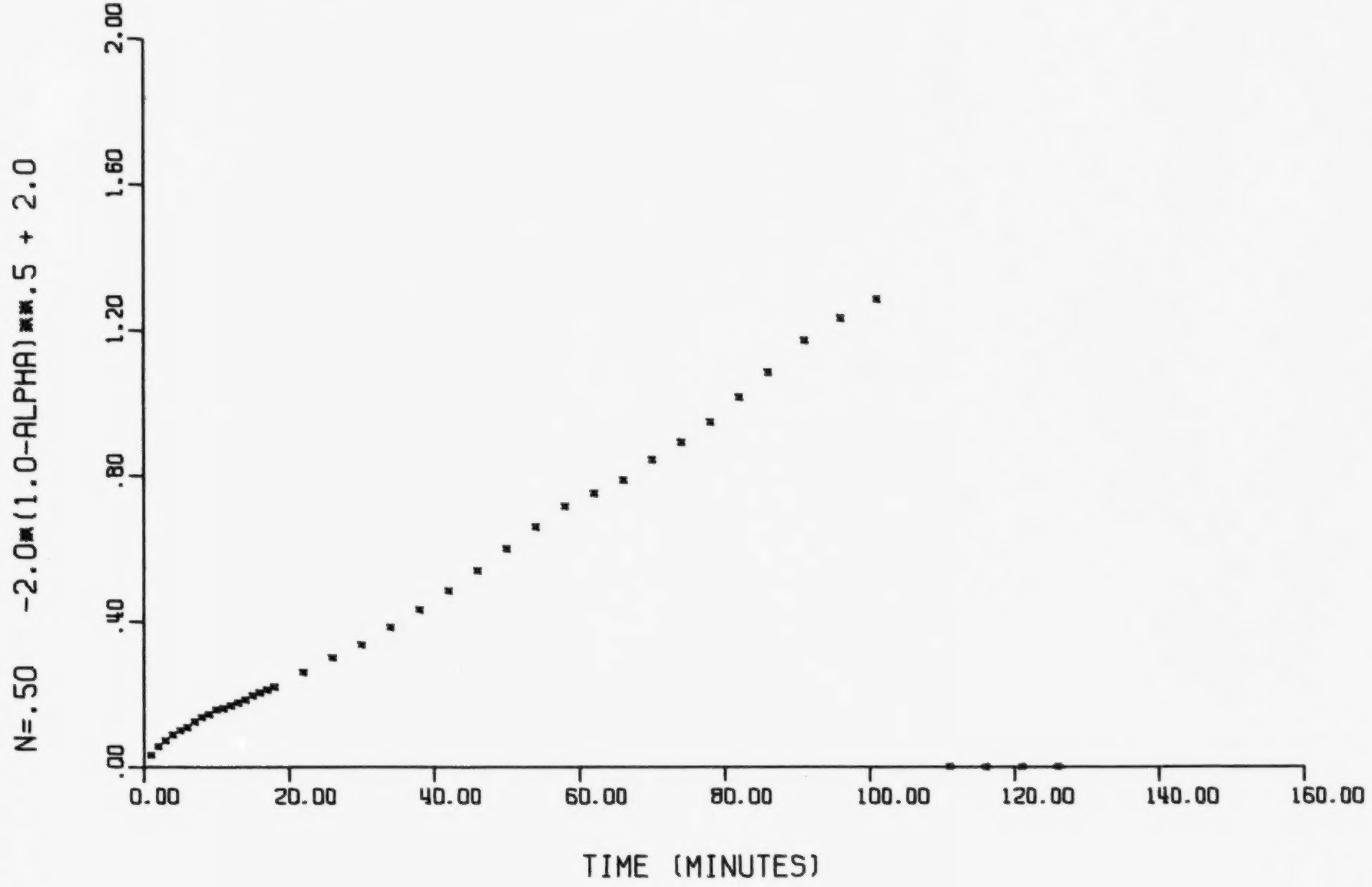

FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C
N=0.0 ALPHA
.00
.20
.40
.60
.80
1.00
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
TIME (MINUTES)
24 MAR 69
TRACOR

FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



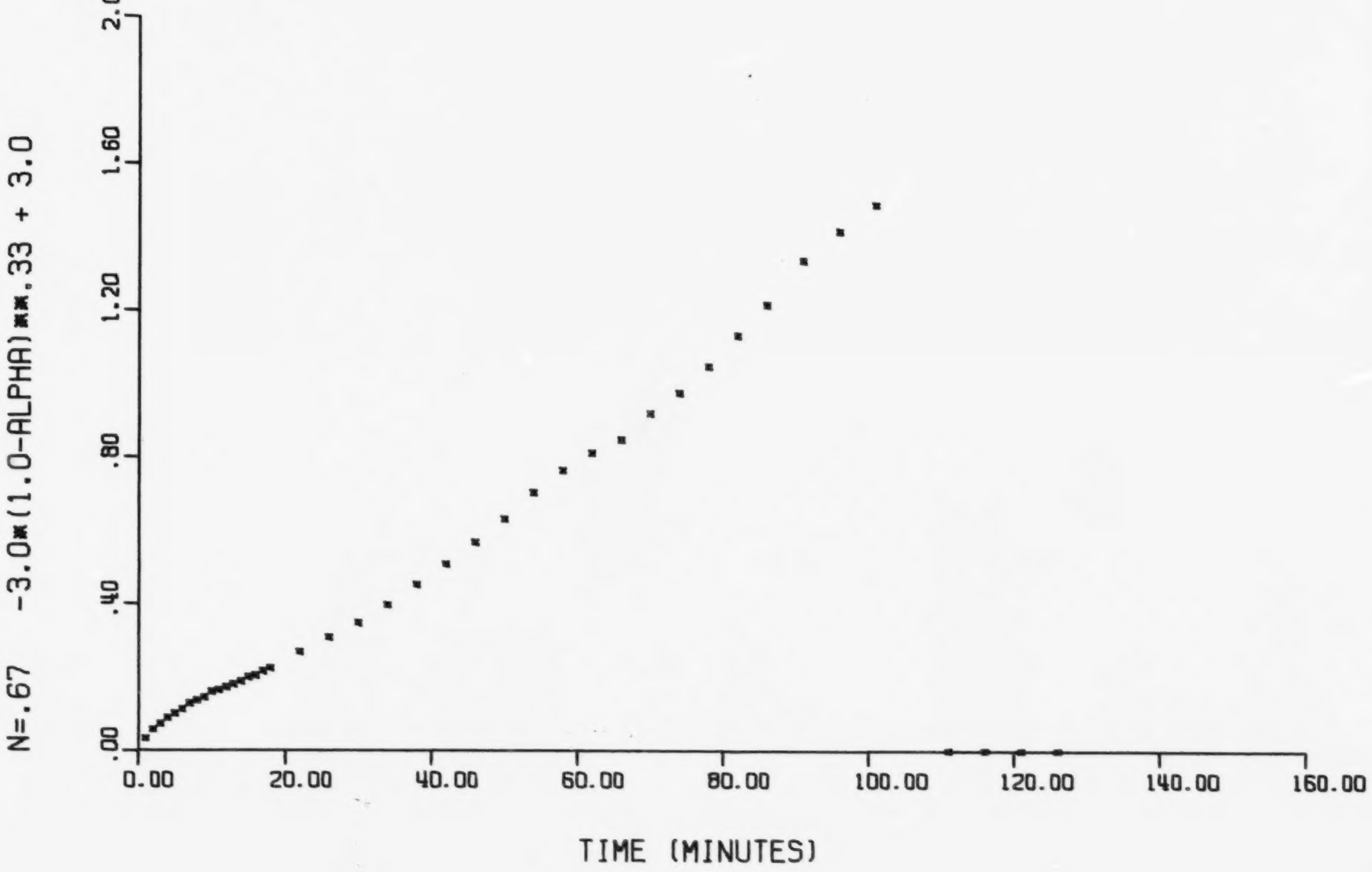
24 MAR 69

FE2O3 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



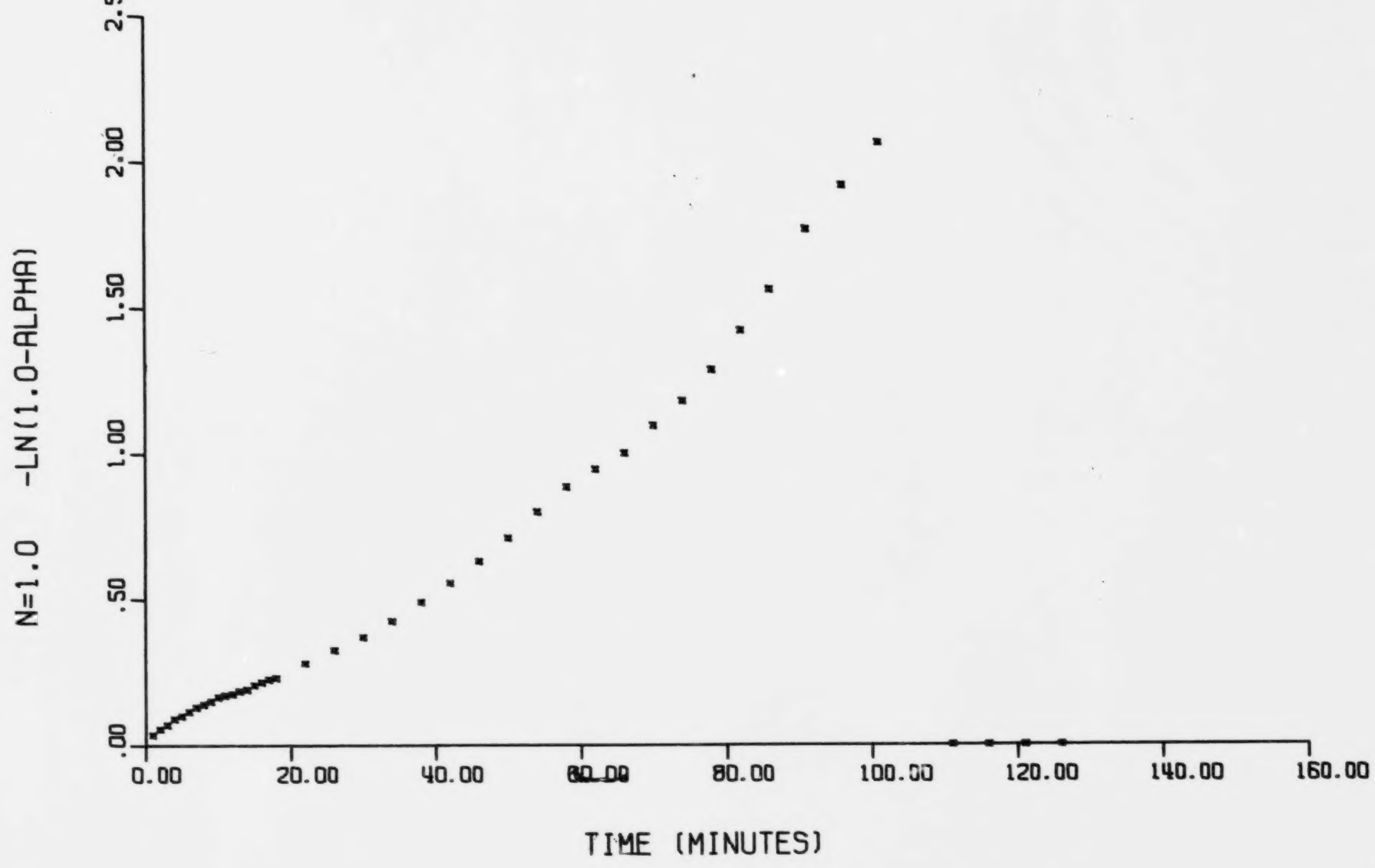
24 MAR 69

FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



24 MAR 69

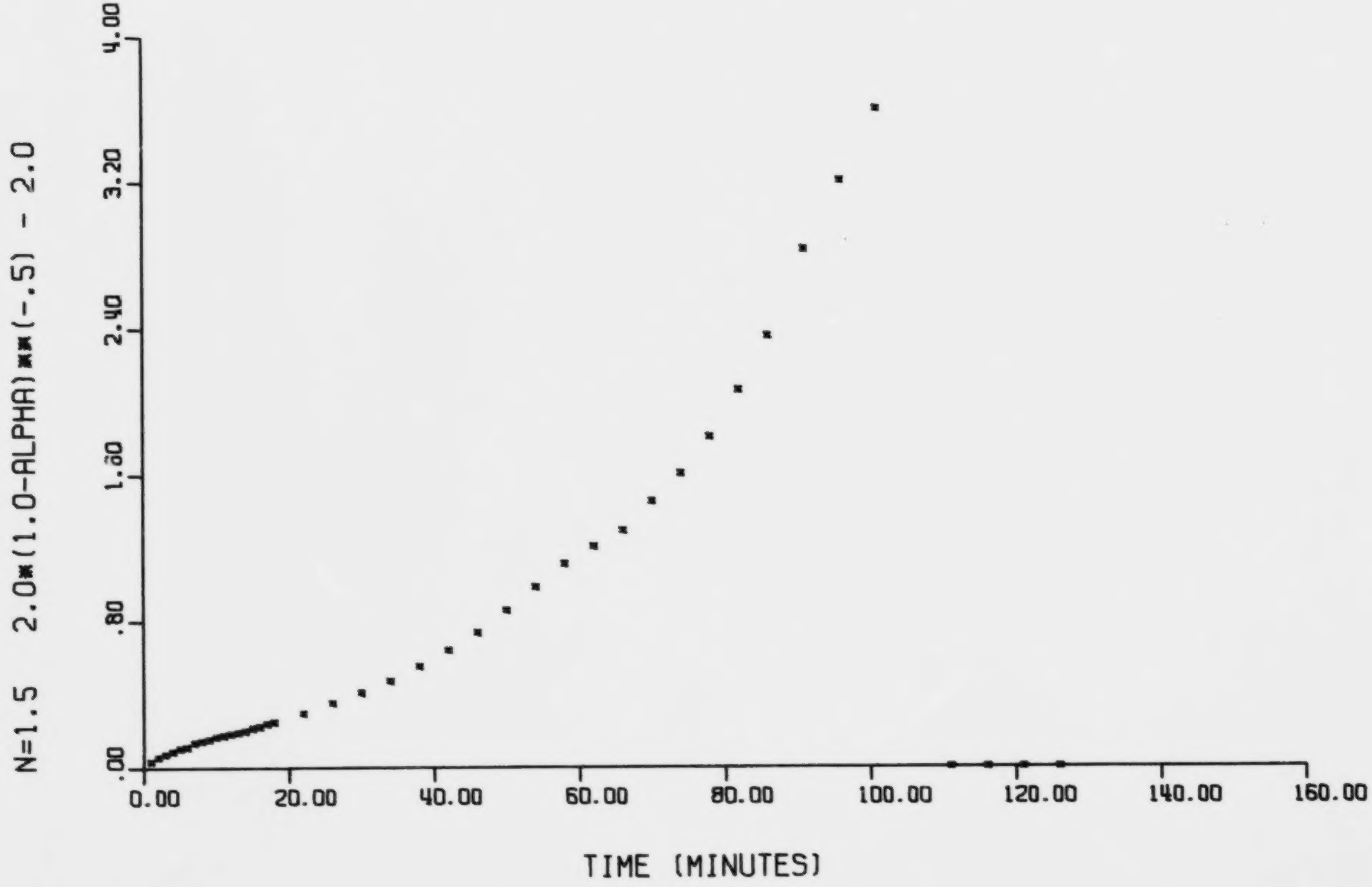
FE2O3 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



24 MAR 69

TRACOR

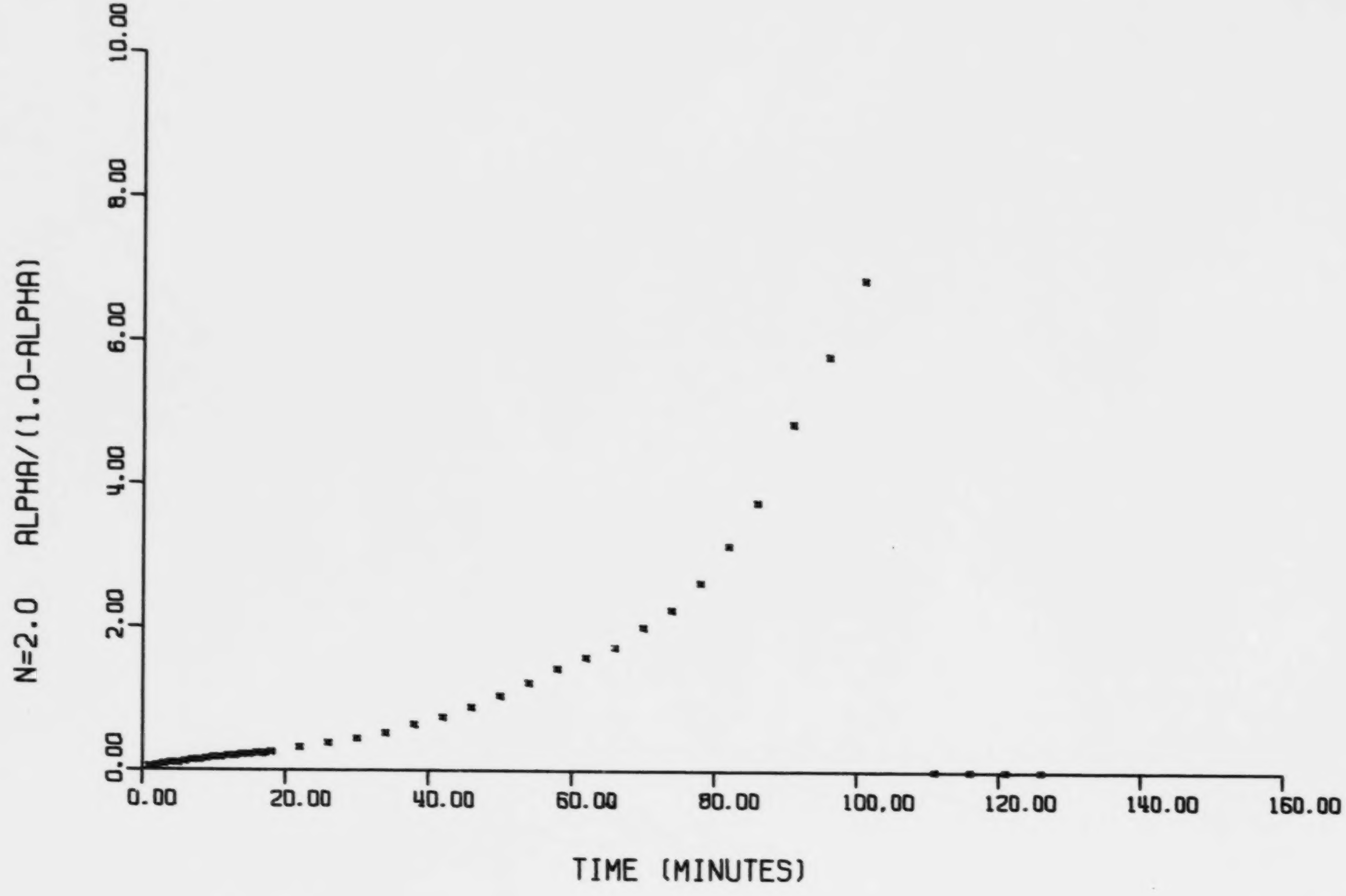
FE2O3 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



24 MAR 69

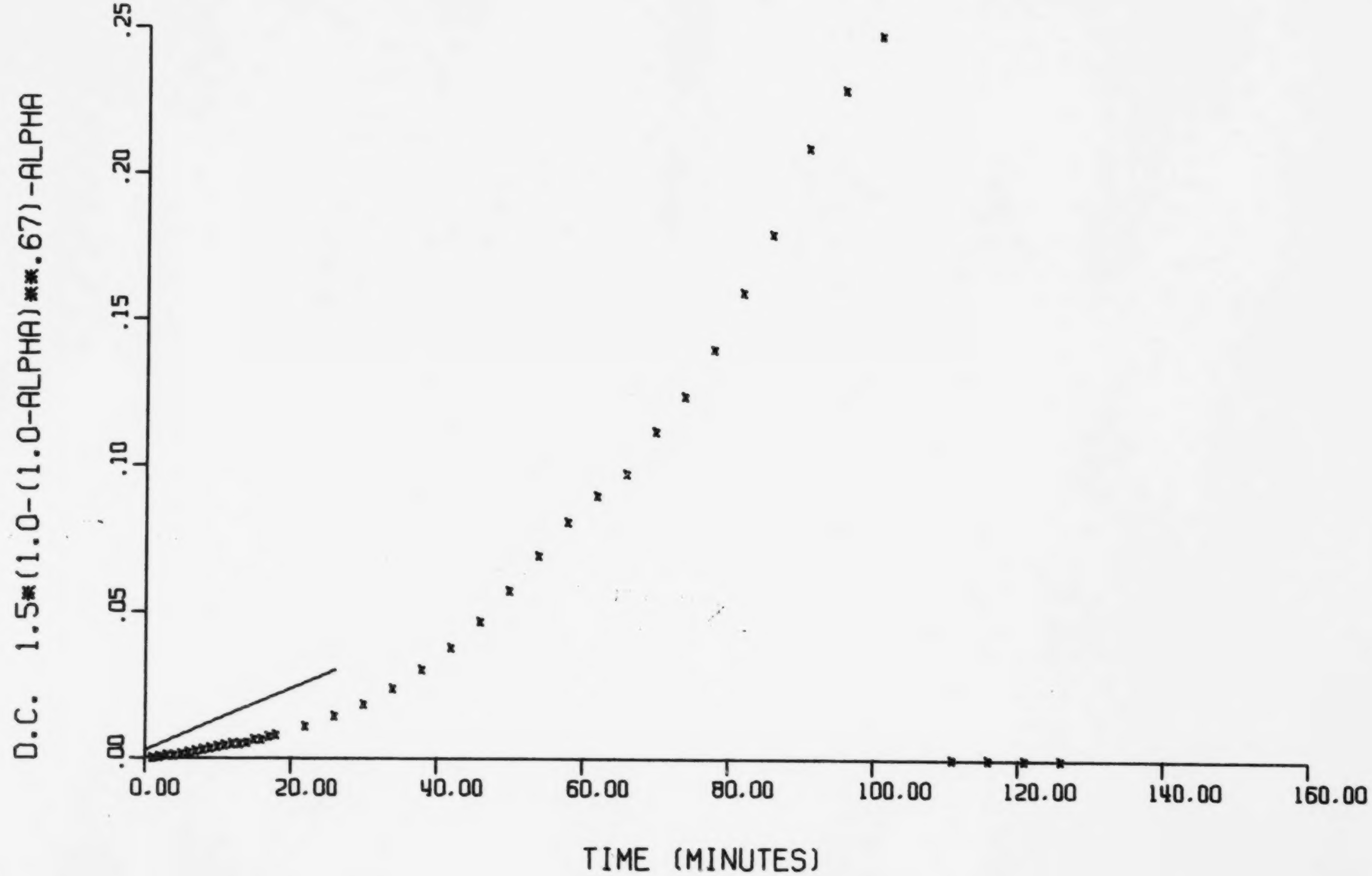
TRACOR

FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



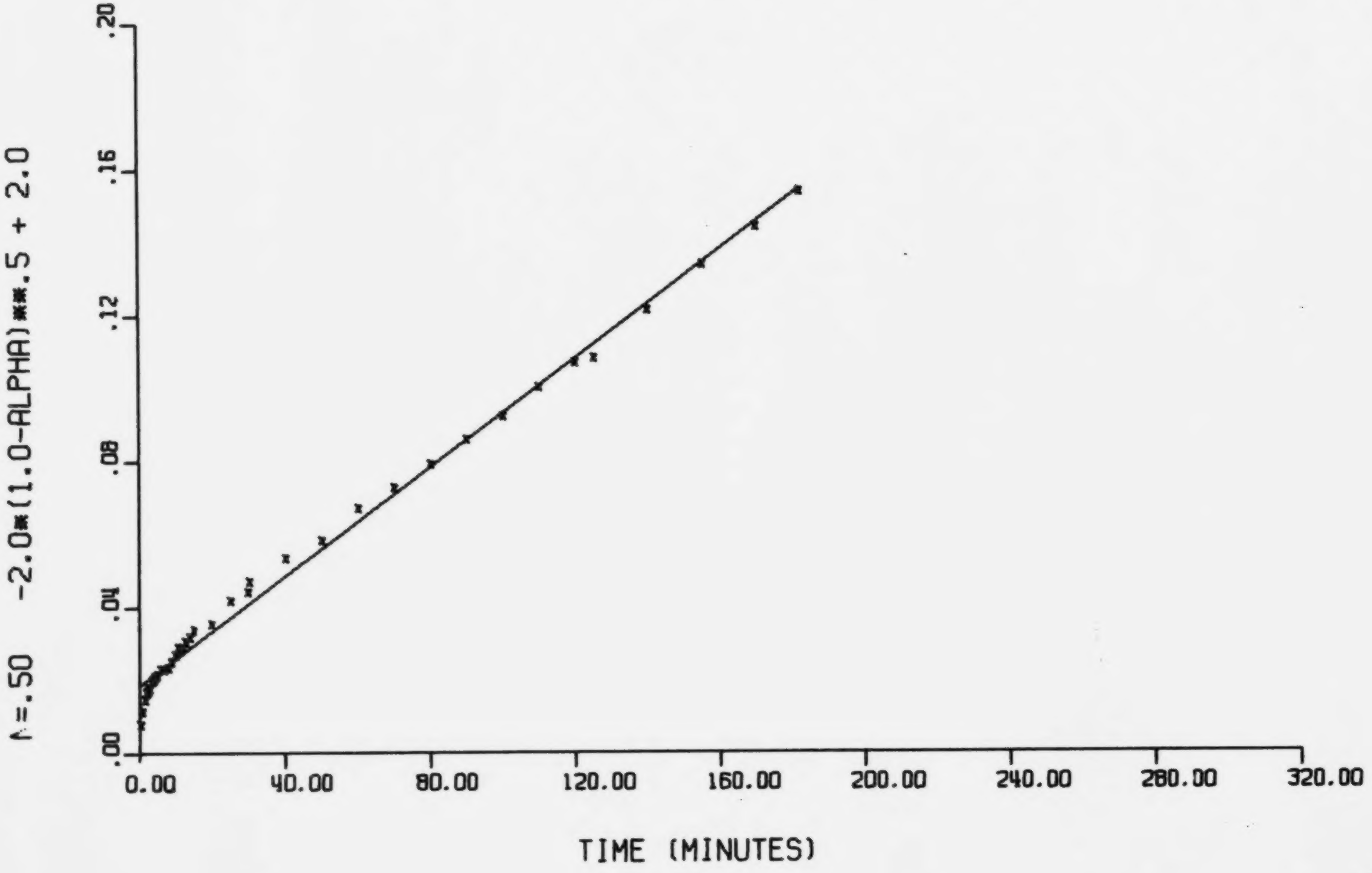
24 MAR 69

FE203 634-45-1
ISO-TGA-1 TEMP = 400 DEG C



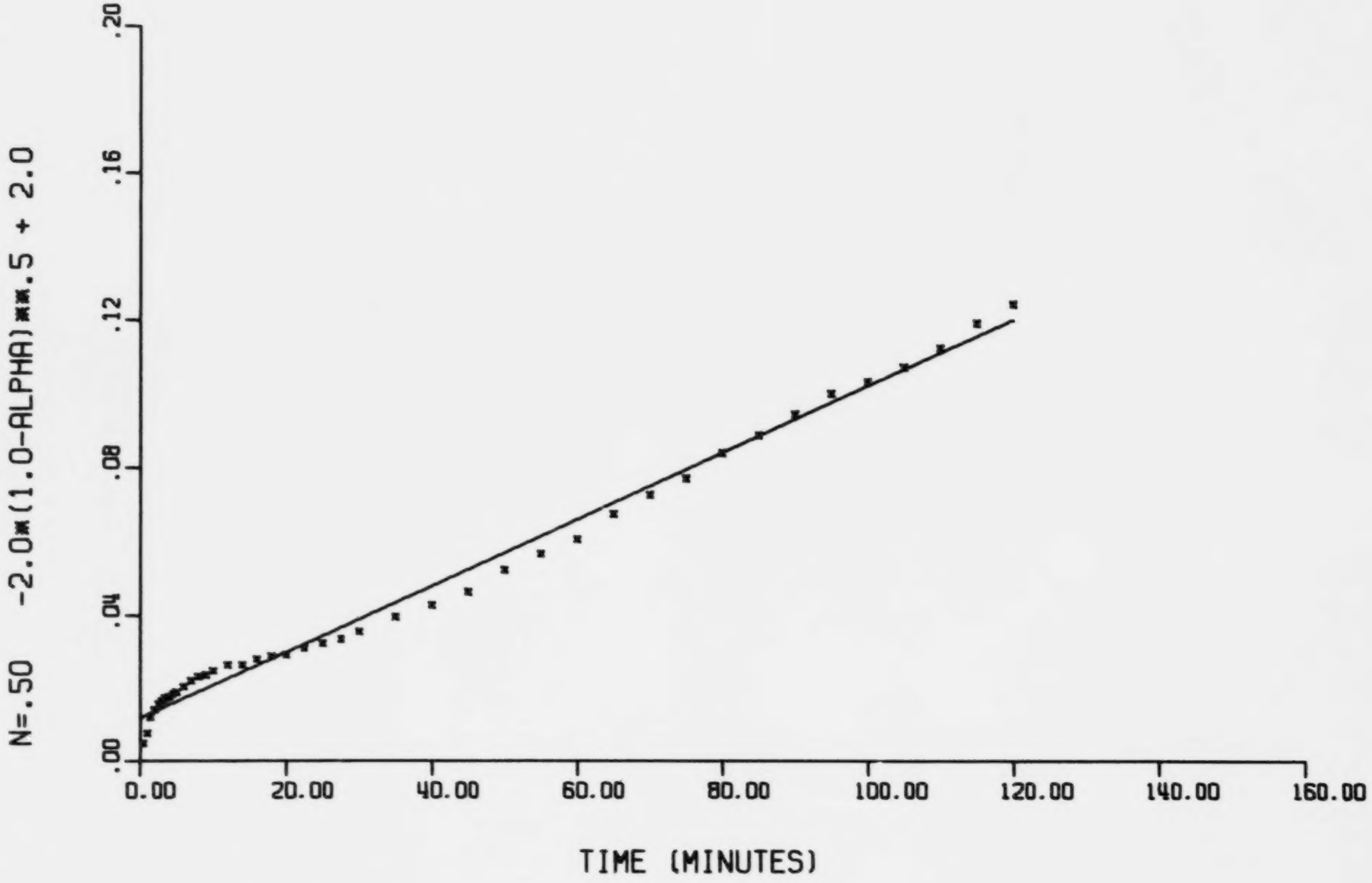
27 MAR 69

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



18 APR 69

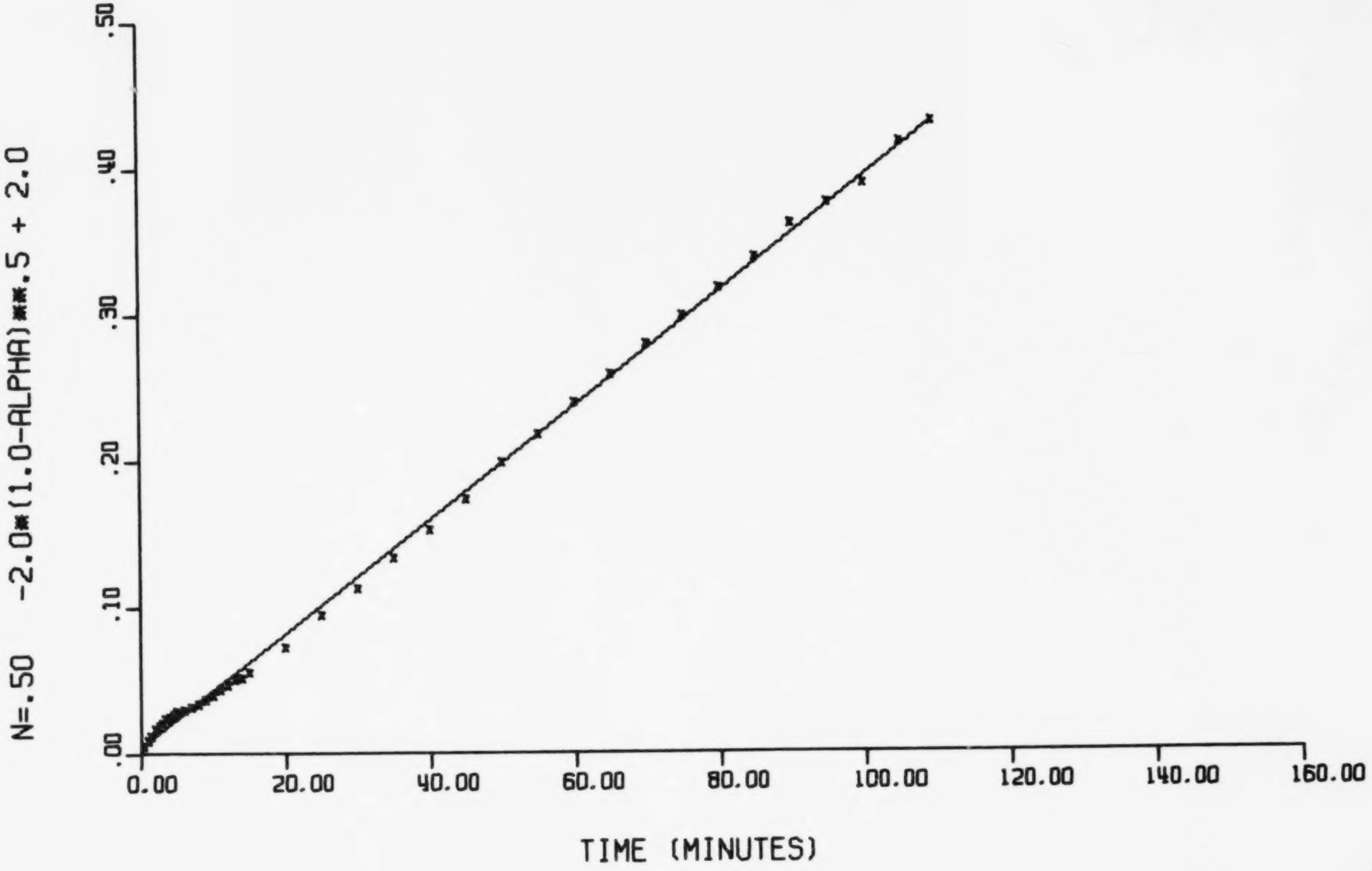
NIO 634-65-2
ISO-TGA-2 TEMP = 432 DEG C



17 JUN 69

TRACOR

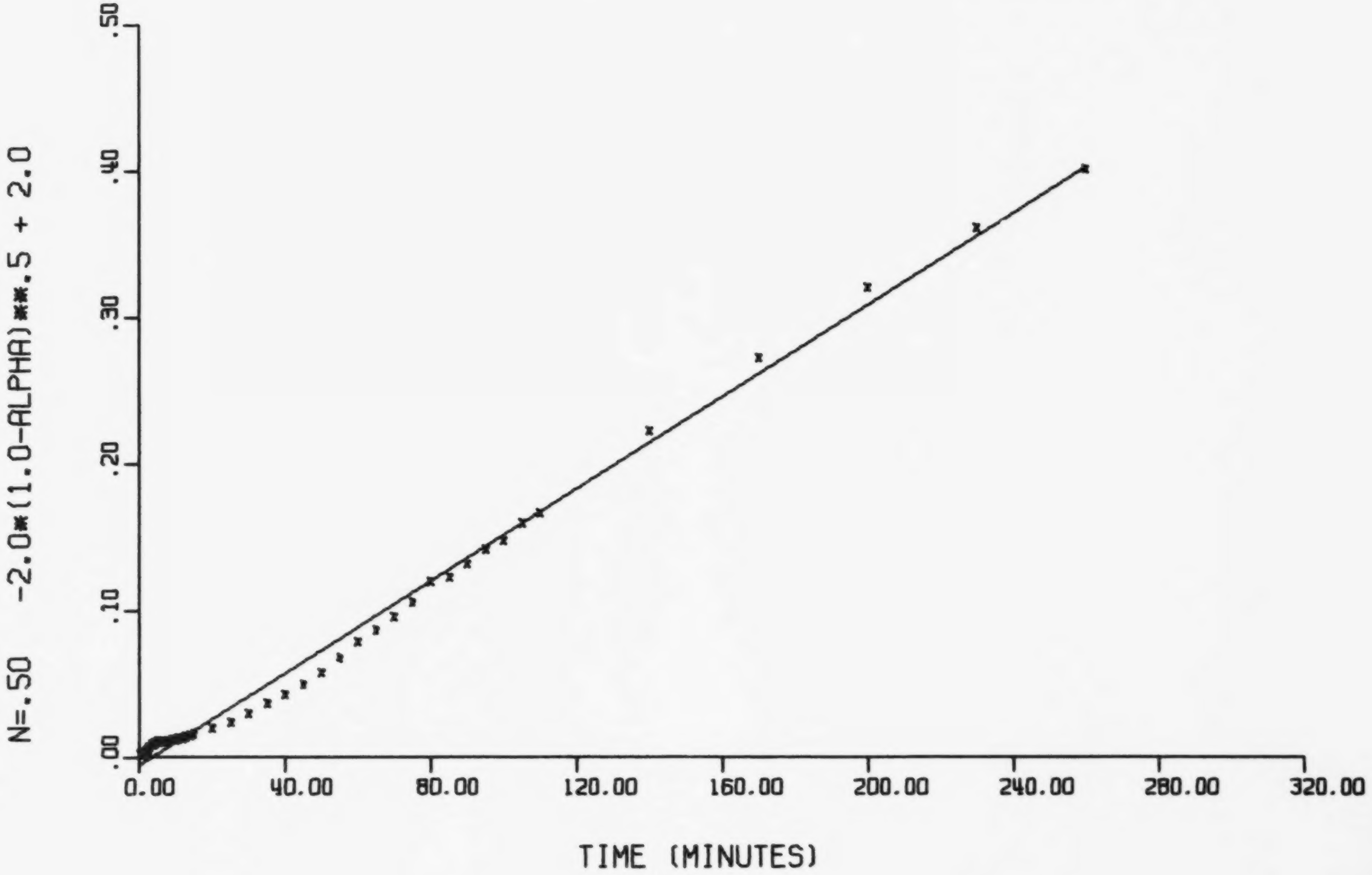
NIO 634-65-2
ISO TGA 2 TEMP = 501 DEG C



18 APR 69

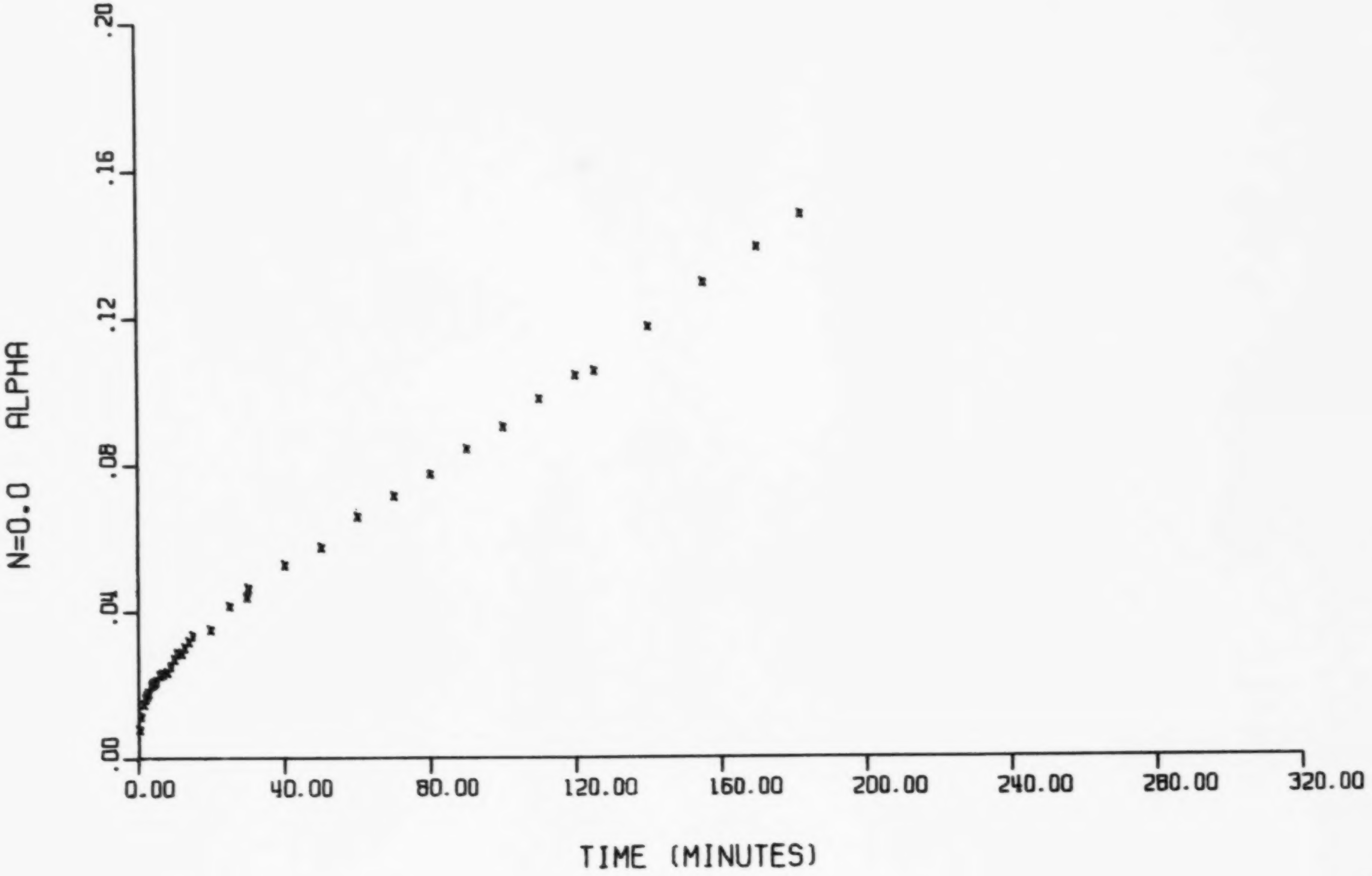
TRACOR

NIO 634-65-2
SO2 CONC 0.124 TEMP = 500 DEG C



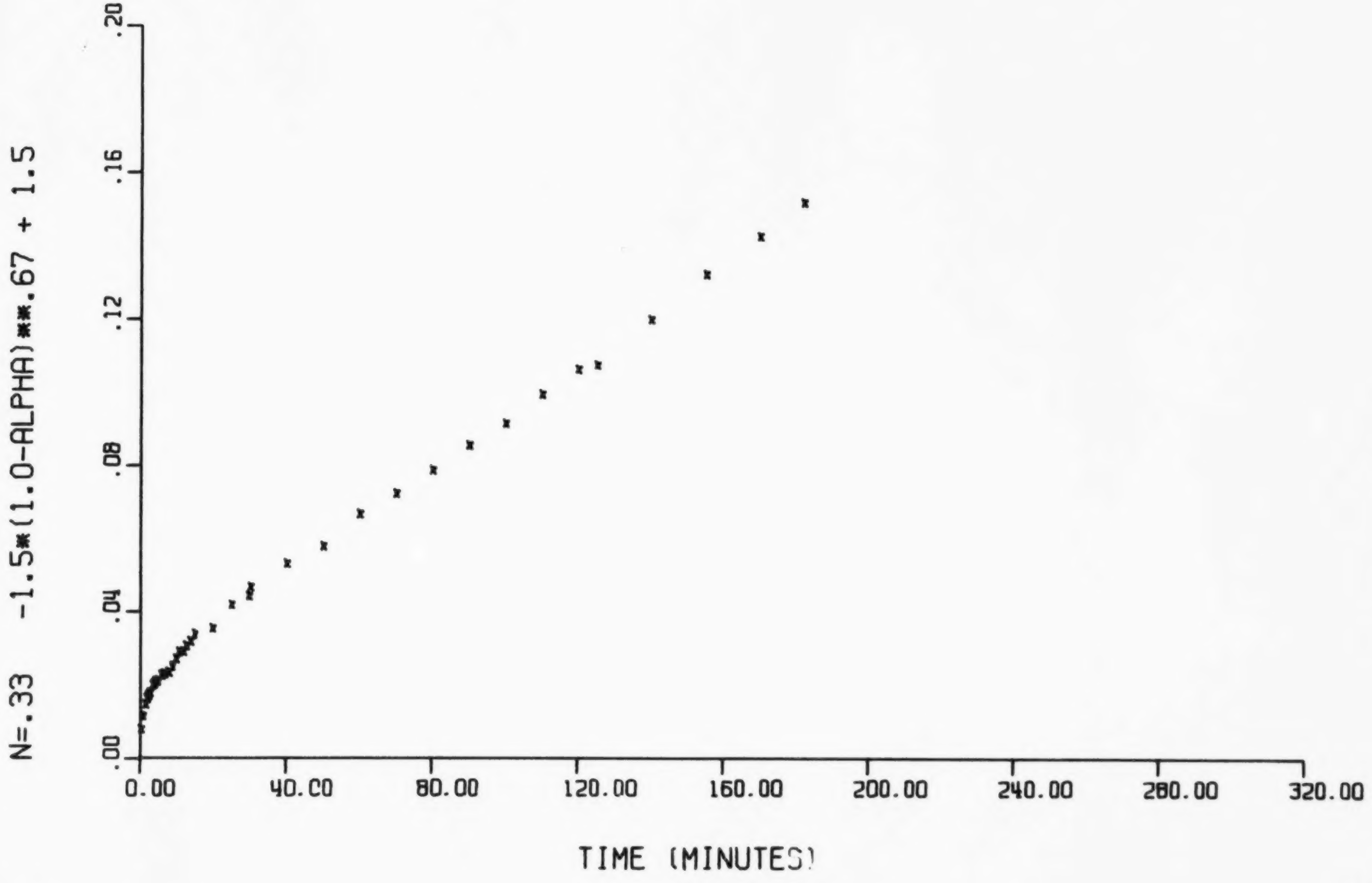
18 APR 69

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



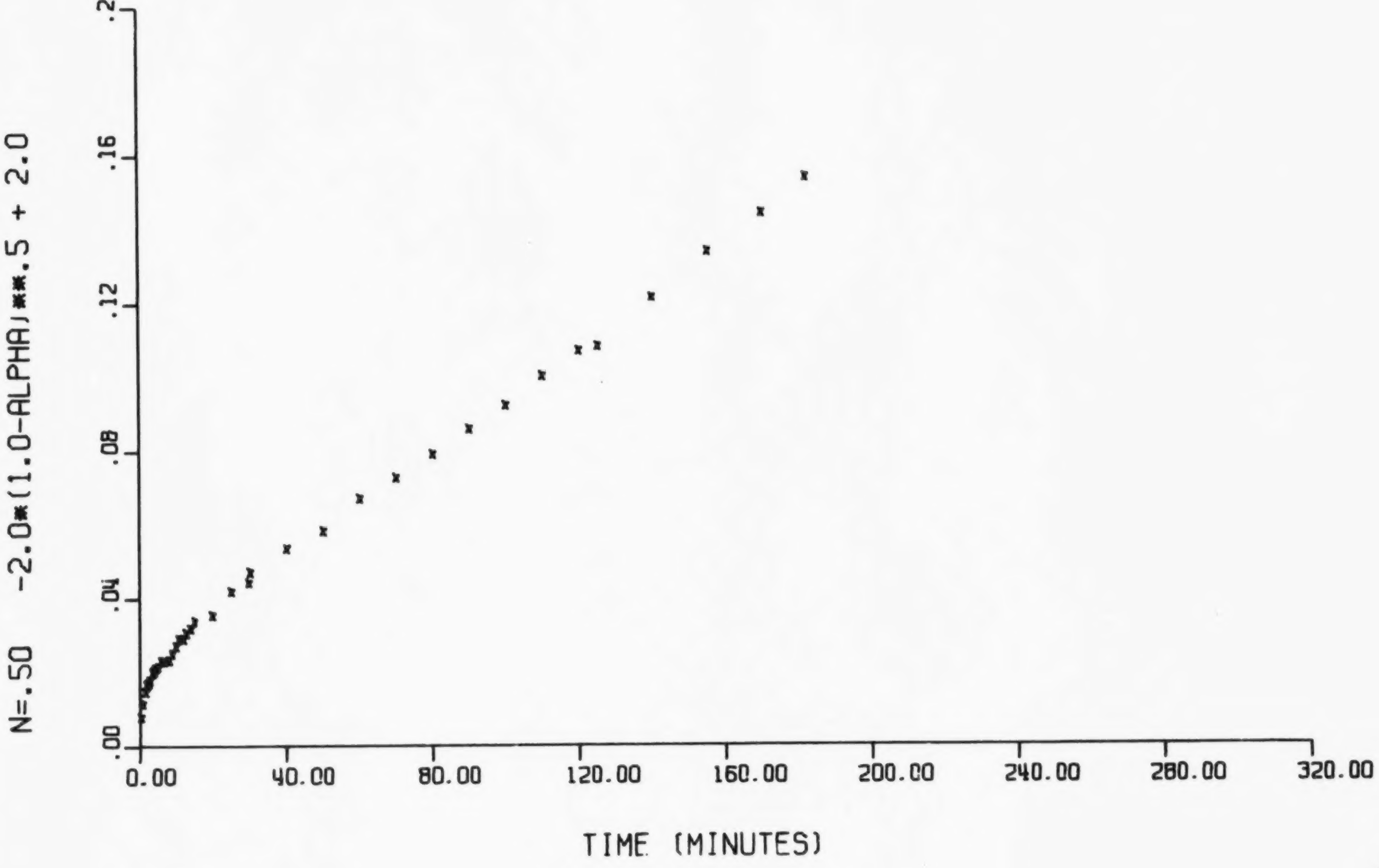
15 APR 69

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

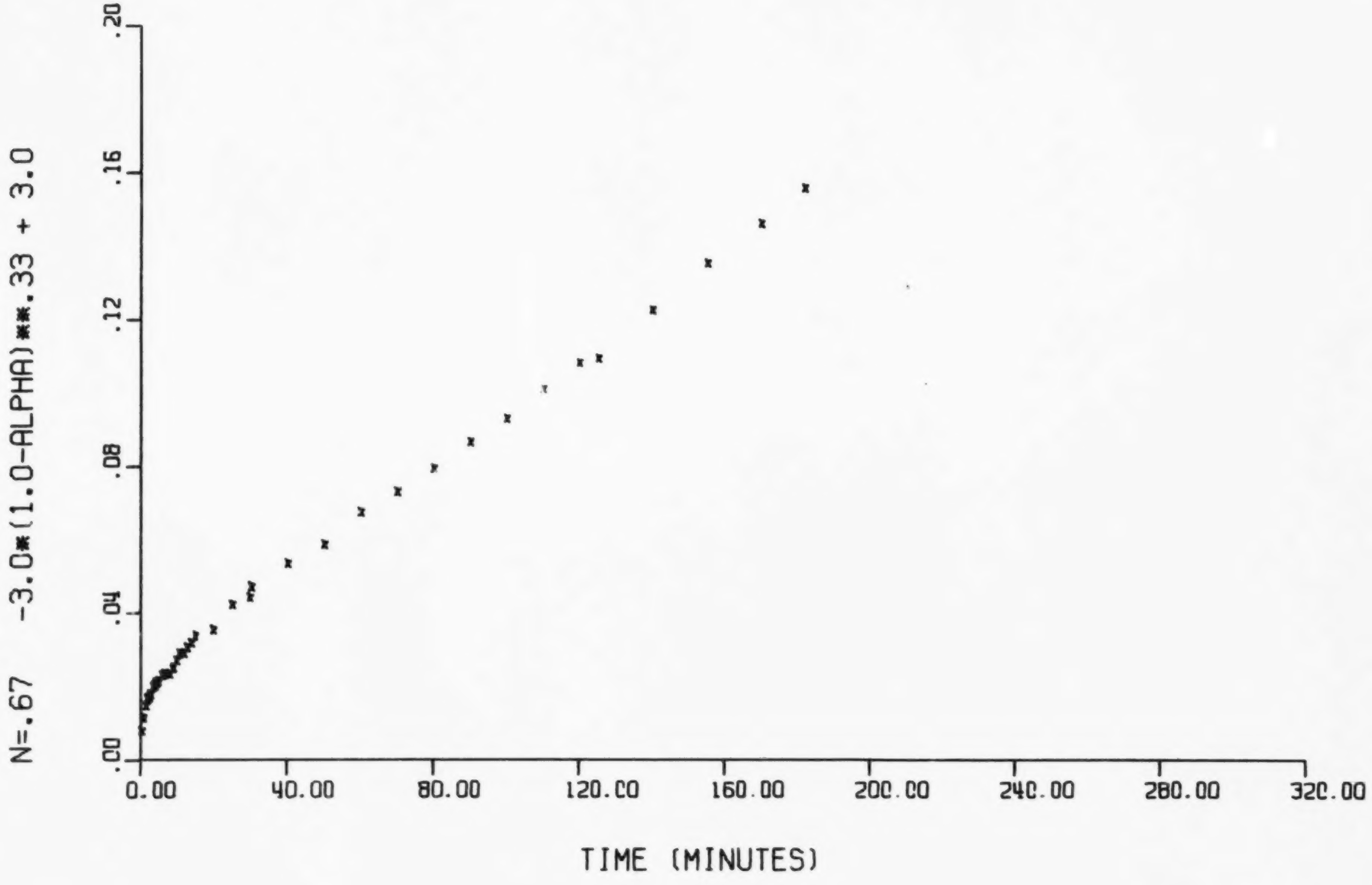
NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

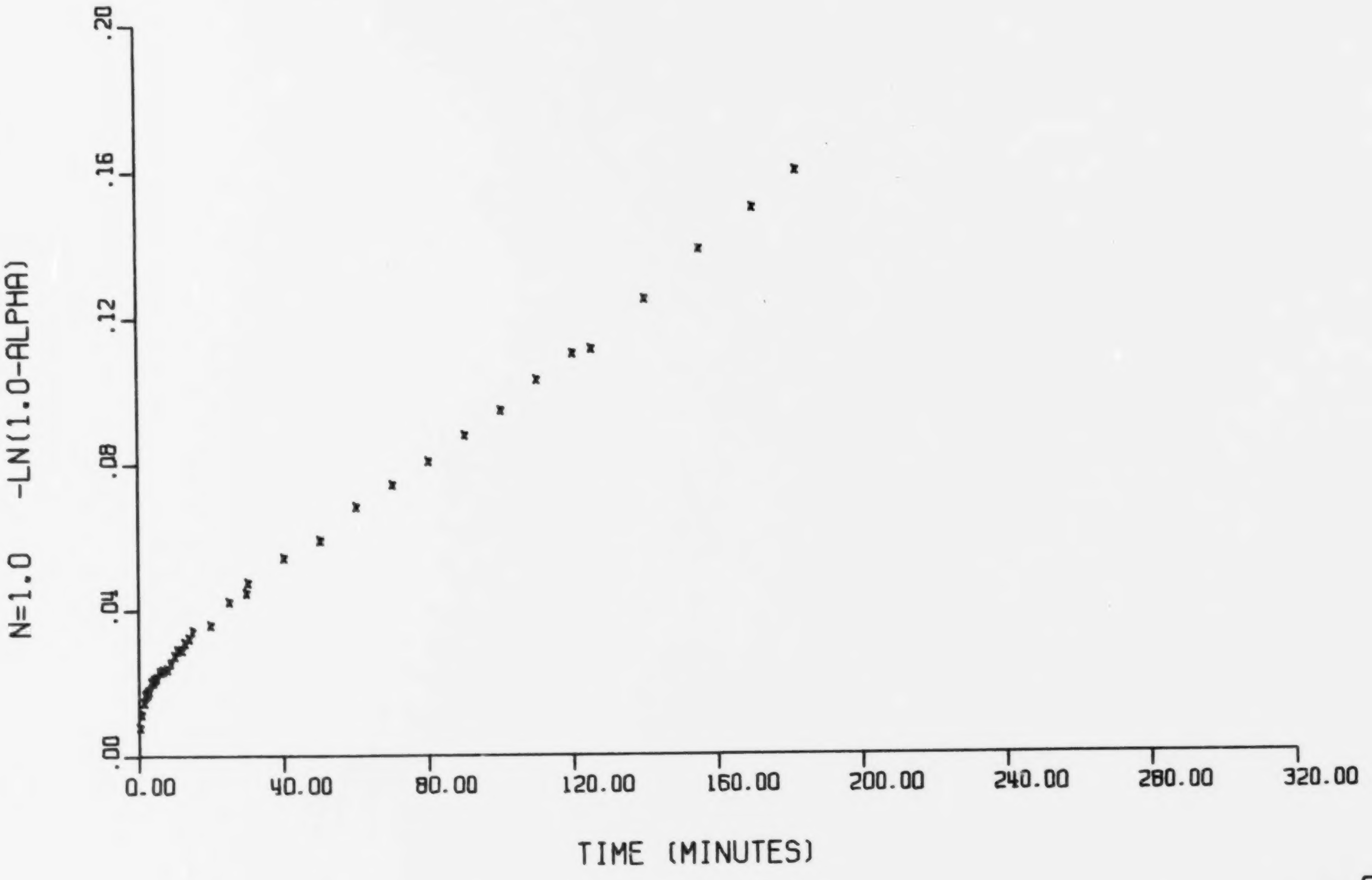
TRACOR

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

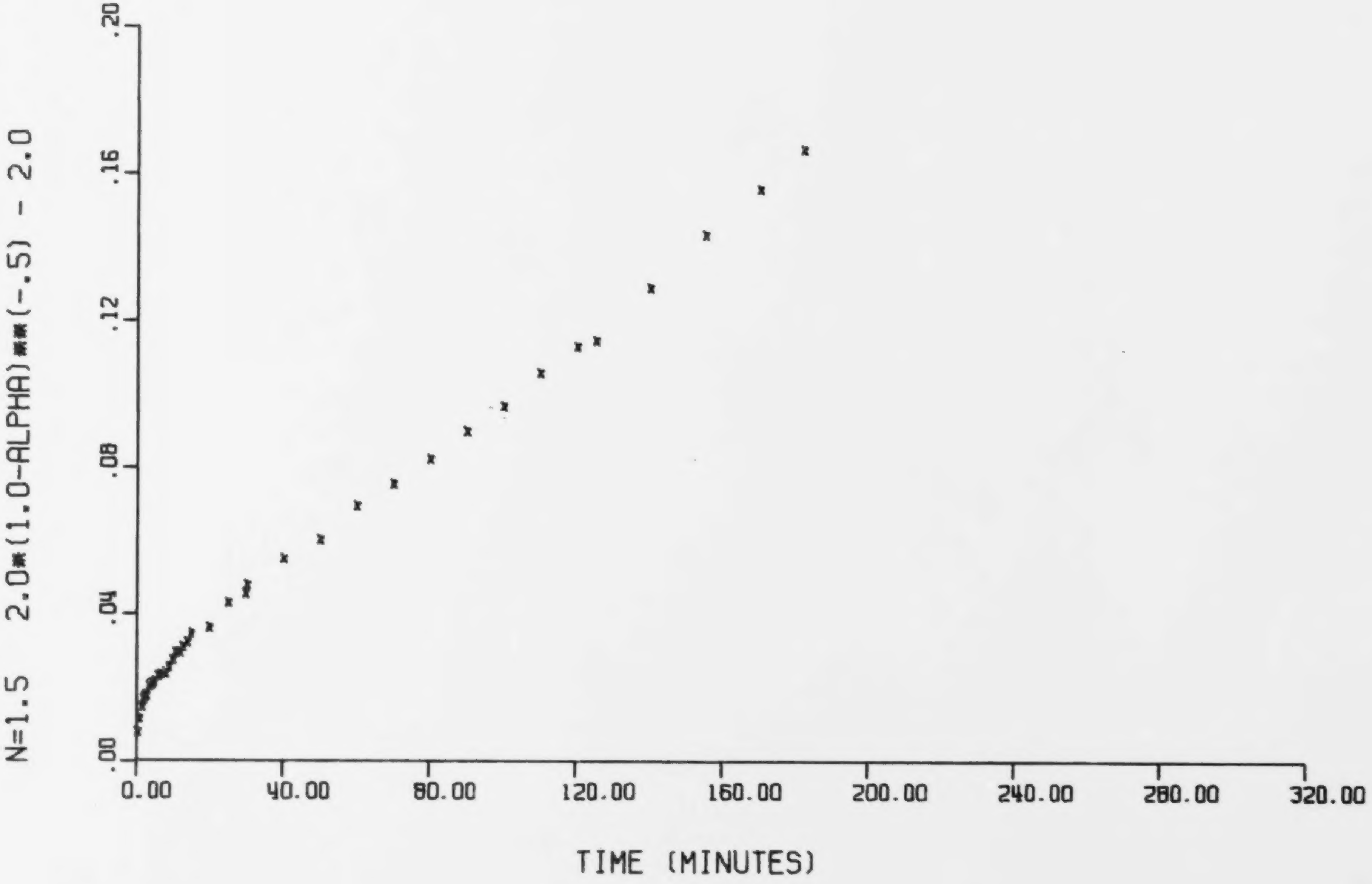
NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

TRACOR

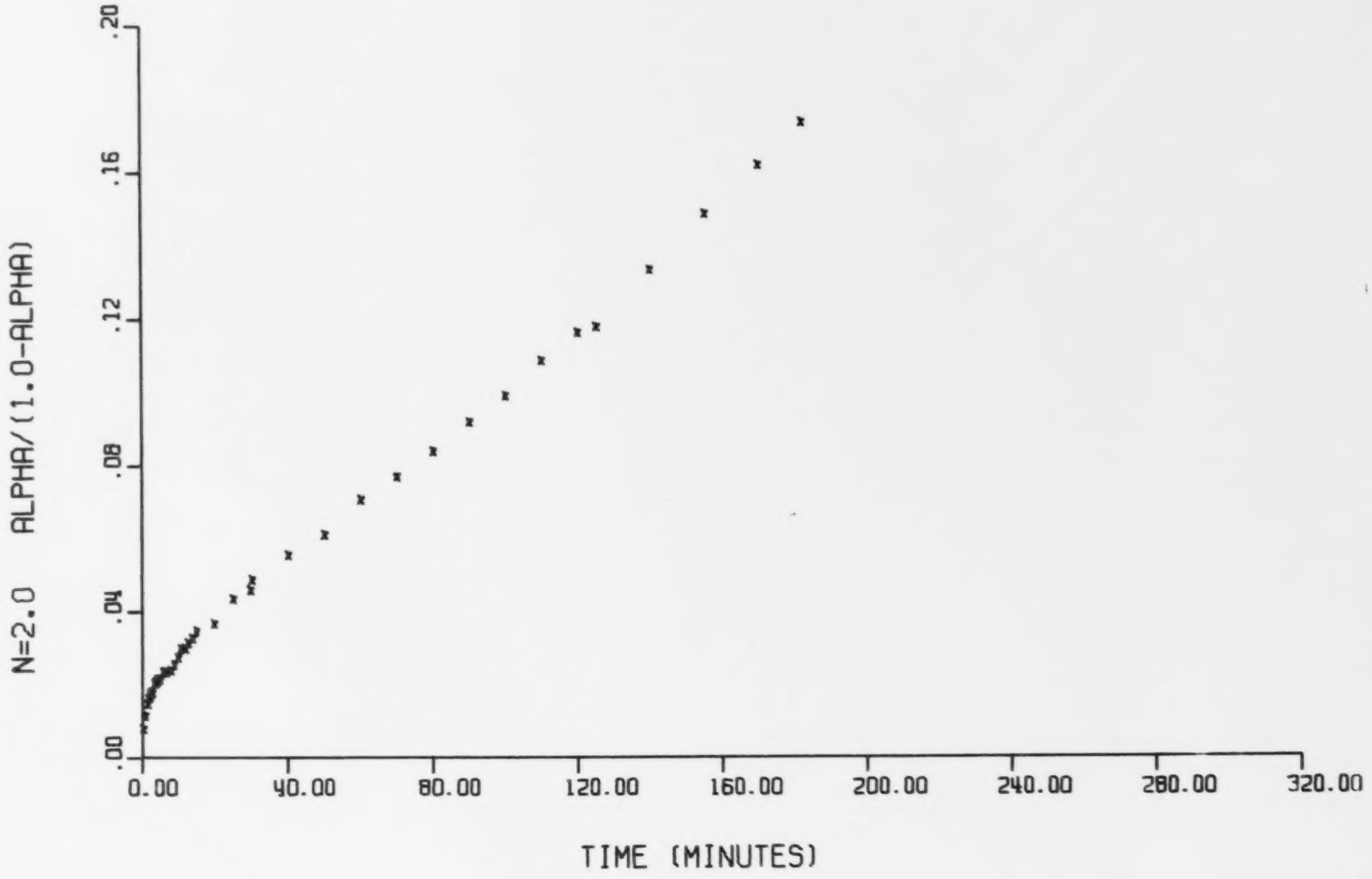
NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

TRACOR

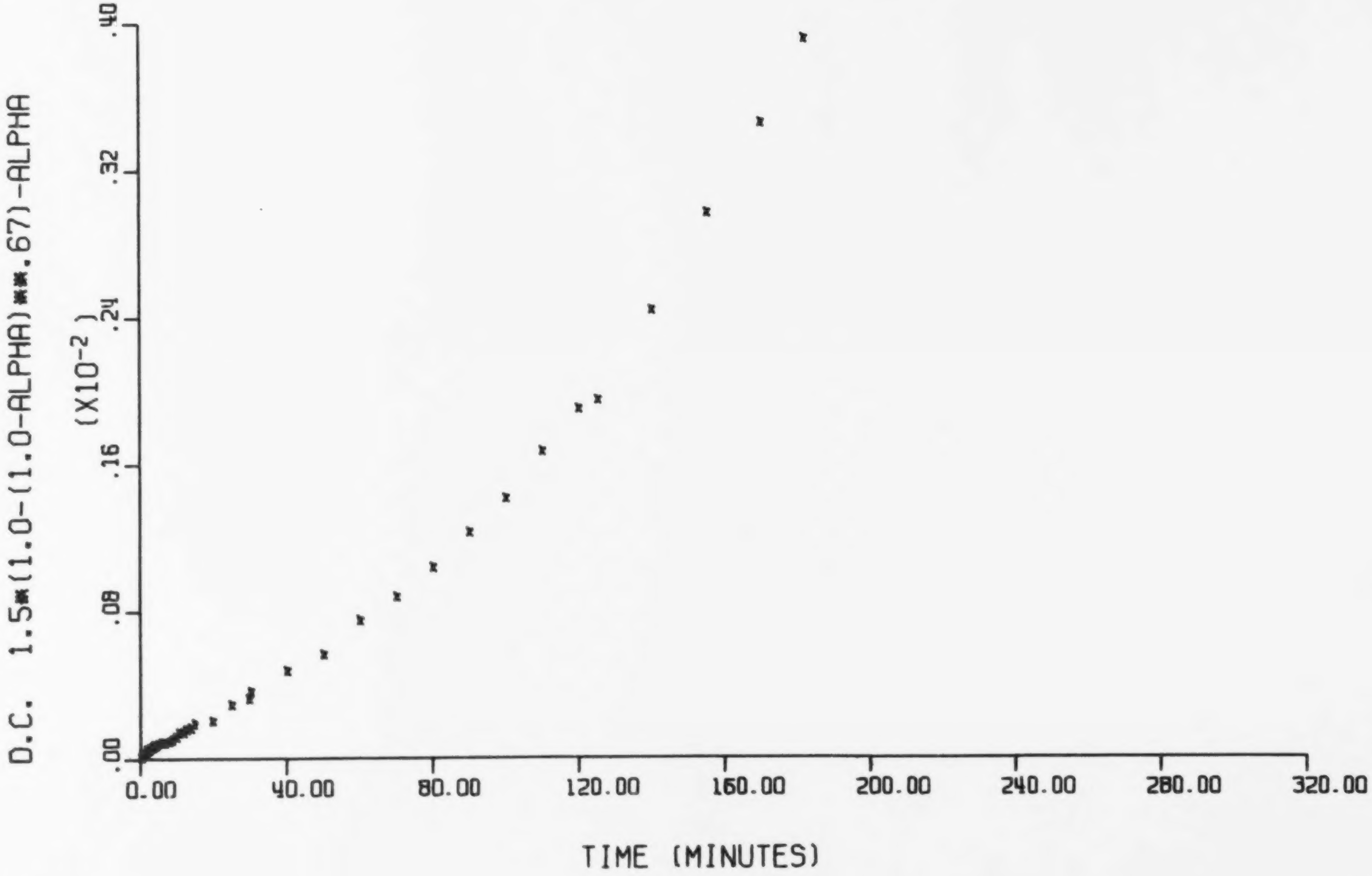
NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

TRACOR

NIO 634-65-2
ISO TGA 1 TEMP = 380 DEG C



15 APR 69

8.2 THERMODYNAMIC, KINETIC, AND ECONOMIC DATA

8.2.4 Economic Calculations for the Best Potential Sorbents

COPPER OXIDE SORBER

```
                                      INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                        2500000.000        DENSITY OF SOLID (LBS/FT**3)            100.000
PARTICLE DIAMETER (INCHES)                    .0300        INLET CONCENT. (MOLE PERCENT)            .00300
REACTION RATE (1/SEC)                      97.50000        OUTLET CONCENT. (MOLE PERCENT)           .00015
RATIO- SUPERFICIAL TO MIN. VEL.               9.000        VOL. WAKE / VOL. BUBBLE                    .320
TEMPERATURE (DEG. F.)                       613.000        FRACTION OF SOLIDS IN BUBBLE               .000
INLET PRESSURE (PSIA)                        14.700


                                     OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                        5155171.000        INITIAL BUBBLE DIAMETER (FEET)             .205
DIAMETER OF BED (FEET)                      136.583        FINAL BUBBLE DIAMETER (FEET)               .328
HEIGHT OF BED (FEET)                          2.675        INITIAL BUBBLE VEL. (FT/SEC)              7.041
HEIGHT OF VESSEL (FEET)                      68.291        FINIAL BUBBLE VEL. (FT/SEC)               7.523
THICKNESS OF SHELL (INCHES)                    .427        MIN. MASS FLUX (LBS/HR-FT**2)            89.422
BED PRESSURE DROP (IN. WATER)                 4.283        MIN. FLUID VOIDAGE                         .458
DISTR. PRESS. DROP (IN. WATER)                1.441        MIN. FLUID VEL. (FT/SEC)                   .652
TOTAL PRESS. DROP (IN. WATER)                 5.724        HOLES/IN.**2 IN DISTR. PLATE              1.055
OUTLET PRESSURE (PSIA)                       14.493        PARTICLE TERMINAL VEL. (FT/SEC)          11.835
WEIGHT OF SORBENT (LBS)                  327088.130        SUPERFICIAL VELOCITY (FT/SEC)             5.866
FRACTION OF SOLIDS IN CLOUD                   2.791        FRACTIONS OF BUBBLES IN BED                .846
FRACTION OF SOLIDS IN EMULSION               -2.619
```

COPPER OXIDE SORBER

```
PAGE   3                                                                          26 JUN 1969
                                     INPUT PARAMETERS FOR SORBER

   INSIDE SHELL DIAMETER (FEET)          136.583          SHELL HEIGHT (FEET)                  68.291
   SHELL THICKNESS (INCHES)                 .427          CURRENT COST INDEX                  279.100


                                   OUTPUT PARAMETERS FOR SORBER SHELL


   WEIGHT OF SHELL (LBS)              1190891.000          LINING COST (DOLLARS)                21410.
   WEIGHT OF HEADS (LBS)              1190891.000          COST OF VESSEL (DOLLARS)            544810.
   WEIGHT OF DISTR. PLATE (LBS)        434771.850          TOTAL COST OF SORBER (DOLLARS)      566220.
   WEIGHT OF VESSEL (LBS)             2816553.700
```

COPPER OXIDE SORBER

```
PAGE 5                                                                         26 JUN 1969
                                    INPUT PARAMETERS FOR CYCLONE


  CYCLONE REMOVAL EFFICIENCY (%)          99.000         PRESSURE DROP (INCHES WATER)          5.000
  FLUID DENSITY (LBS/FT**3)                 .038         SOLID DENSITY (LBS/FT**3)           100.000
  VISCOSITY (LBS/FT-SEC)               .00002013         WALL THICKNESS (INCHES)                .250
  EFFECTIVE TURNS                          3.500         CURRENT COST INDEX                  279.100
  INPUT FLOW RATE (ACFM)             5155171.000         NUMBER OF CYCLONES                       4.


                                    OUTPUT PARAMETERS FOR CYCLONE


                                    INDIVIDUAL CYCLONE PARAMETERS


  INPUT FLOW RATE (ACFM)             1288792.700         INLET VELOCITY (FT/SEC)              73.969
  CYCLONE DIAMETER (FEET)                 48.202         CYCLONE WEIGHT (LBS)             363394.790
  PART. SIZE (MICRONS)- 99.% EFF.         59.800         COST OF EACH CYCLONE (DOLLARS)      139578.
  PART. SIZE (MICRONS)- 50% EFF.          35.370

  TOTAL COST OF ALL CYCLONE UNITS        558312.
```

COPPER OXIDE SORBER

```
                              INPUT VARIABLES FOR FAN COST

COST INDEX AS OF MAY 5,1969          279.100        TOTAL FAN CAPACITY (ACFM)          5155171.000
FAN SPEED (RPM)                     1200.000        AIR DENSITY (LBS/FT**3)                   .038
OVERALL EFFICIENCY                      .850        FAN PRESSURE DROP (IN. WATER)           10.724
NUMBER OF FAN UNITS                       1.


                         FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                              INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)              5155170.900        WHEEL DIAMETER (INCHES)                 91.910
DRIVER BRAKE HORSEPOWER            10211.382        FAN COST (DOLLARS)                      44245.
ACTUAL DRIVER HORSEPOWER           14322.374        MOTOR COST (DOLLARS)                   147006.
FRACTIONAL CAPACITY PER FAN            1.000        EACH FAN UNIT COST (DOLLARS)           191251.

KILOWATTS REQUIRED BY DRIVER(S)     7614.752        COST - ALL FAN UNITS (DOLLARS)         191251.
```

COPPER OXIDE SORBER

26 JUN 1969

SO2 REMOVAL FROM FLUE GAS
CATEGORY
DRY METAL OXIDES
CAPITAL COST ESTIMATE SUMMARY
CASE NO. 104.

NAME OF PROCESS
TRACOR

NAME OF EQUIPMENT
SORPTION UNIT

FLUE GAS RATE 2.5 MMSCFM

MW 1400.0

	ITEM	COST- THOU. $	% OF TOTAL
1.	PURCHASED EQUIPMENT	1315.8	19.22
2.	ERECTION LABOR	328.9	4.80
3.	FOUNDATION & PLATFORMS	236.8	3.46
4.	PIPING	986.8	14.41
5.	INSTRUMENTS	197.4	2.88
6.	INSULATION	105.3	1.54
7.	ELECTRICAL	131.6	1.92
8.	BUILDINGS	328.9	4.80
9.	LAND & YARD IMPROVEMENTS	171.1	2.50
10.	UTILITIES	526.3	7.69
11.	PHYSICAL-PLANT COST	4328.9	63.23
12.	ENGINEERING & CONSTRUCTION	868.4	12.68
13.	DIRECT PLANT COST	5197.3	75.92
14.	CONTRACTOR-S FEE	250.0	3.55
15.	CONTINGENCY	776.3	11.34
16.	FIXED CAPITAL COST	6223.7	90.91
17.	WORKING CAPITAL	622.4	9.09
	TOTAL INVESTMENT	6846.0	100.00
18.	CAPITAL REQUIREMENTS $/KW CAPACITY	4.9	

COPPER OXIDE SORBER

```
                         SO2 REMOVAL FROM FLUE GAS
                                 CATEGORY
                             DRY METAL OXIDES

                      OPERATING COST ESTIMATE SUMMARY
                   BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

             NAME OF PROCESS                         NAME OF EQUIPMENT
                TRACOR                                 SORPTION UNIT

     FLUE GAS RATE    2.5 MMSCFM                                         MW 1400.0
                           FIXED CAPITAL COST    6223652.1

-----------------------------------------------------------------------------------

                 ITEM                                   COST- THOU. $      % OF TOTAL
                 ----                                   -------------      ----------

      1.  RAW MATERIALS & CHEMICALS                          693.4            32.09
      2.  DIRECT LABOR                                        54.0             2.50
      3.  SUPERVISION                                         27.4             1.27
      4.  MAINTENANCE, 5% OF FIXED CAPITAL                   311.2            14.40
      5.  SUPPLIES, 15% OF MAINTENANCE                        46.7             2.16
      6.  UTILITIES                                          253.5            11.73
      7.  OTHER                                             -270.0           -12.49
      8.        TOTAL DIRECT COST                           1116.1            51.65
      9.  PAYROLL BURDEN, 20% OF 2 & 3                        16.3              .75
     10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                 219.6            10.16
     11.  PACK & SHIP                                           .0              .00
     12.  WASTE DISPOSAL                                        .0              .00
     13.  OTHER                                                 .0              .00
     14.        TOTAL INDIRECT COST                          235.9            10.92
     15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR             622.4            28.80
     16.  TAXES, 2% OF FIXED CAPITAL                         124.5             5.76
     17.  INSURANCE, 1% OF FIXED CAPITAL                      62.2             2.88
     18.  OTHER                                                 .0              .00
     19.        TOTAL FIXED COST                             809.1            37.44

     20.  TOTAL OPERATING COST                              2161.1           100.00
     21.  COST:  $/TON OF COAL                .672
                  MIL/KWH                     .195
```

```
PAGE  1                          COPPER OXIDE REGENERATOR                                  25 JUN 1969
                                 INPUT FOR FLUIDIZED BED

FLOW RATE (SCFM)                       111500.000        DENSITY OF SOLID (LBS/FT**3)          100.000
PARTICLE DIAMETER (INCHES)                  .0300        INLET CONCENT. (MOLE PERCENT)        10.00000
REACTION RATE (1/SEC)                    10.00000        OUTLET CONCENT. (MOLE PERCENT)        1.00000
RATIO- SUPERFICIAL TO MIN. VEL.             9.000        VOL. WAKE / VOL. BUBBLE                  .320
TEMPERATURE (DEG. F.)                    1377.000        FRACTION OF SOLIDS IN BUBBLE             .000
INLET PRESSURE (PSIA)                      14.700


                                 OUTPUT FROM FLUIDIZED BED

FLOW RATE (ACFM)                       394029.950        INITIAL BUBBLE DIAMETER (FEET)           .229
DIAMETER OF BED (FEET)                     43.110        FINAL BUBBLE DIAMETER (FEET)             .328
HEIGHT OF BED (FEET)                        2.348        INITIAL BUBBLE VEL. (FT/SEC)            5.928
HEIGHT OF VESSEL (FEET)                    21.555        FINIAL BUBBLE VEL. (FT/SEC)             6.310
THICKNESS OF SHELL (INCHES)                  .250        MIN. MASS FLUX (LBS/HR-FT**2)          40.074
BED PRESSURE DROP (IN. WATER)               7.036        MIN. FLUID VOIDAGE                       .465
DISTR. PRESS. DROP (IN. WATER)              2.361        MIN. FLUID VEL. (FT/SEC)                 .500
TOTAL PRESS. DROP (IN. WATER)               9.397        HOLES/IN.**2 IN DISTR. PLATE             .483
OUTLET PRESSURE (PSIA)                     14.361        PARTICLE TERMINAL VEL. (FT/SEC)        14.207
WEIGHT OF SORBENT (LBS)                 53525.159        SUPERFICIAL VELOCITY (FT/SEC)           4.500
FRACTION OF SOLIDS IN CLOUD                 1.567        FRACTIONS OF BUBBLES IN BED              .767
FRACTION OF SOLIDS IN EMULSION             -1.326
```

```
PAGE  3                              COPPER OXIDE REGENERATOR                                    26 JUN 1969
                                        INPUT PARAMETERS

  INSIDE SHELL DIAMETER (FEET)                 43.110        SHELL HEIGHT (FEET)                        21.555
  SHELL THICKNESS (INCHES)                       .250        CURRENT COST INDEX                        279.100


                                   OUTPUT PARAMETERS FOR SORBER SHELL


  WEIGHT OF SHELL (LBS)                     69510.444        LINING COST (DOLLARS)                       2133.
  WEIGHT OF HEADS (LBS)                     69510.444        COST OF VESSEL (DOLLARS)                   48208.
  WEIGHT OF DISTR. PLATE (LBS)              43313.694        TOTAL COST OF SORBER (DOLLARS)             50341.
  WEIGHT OF VESSEL (LBS)                   182334.580
```

COPPER OXIDE REGENERATOR

```
                                                                                          26 JUN 1969
                                         INPUT PARAMETERS FOR CYCLONE

   CYCLONE REMOVAL EFFICIENCY (%)             98.000          PRESSURE DROP (INCHES WATER)              5.000
   FLUID DENSITY (LBS/FT**3)                    .022          SOLID DENSITY (LBS/FT**3)               100.000
   VISCOSITY (LBS/FT-SEC)                  .00001830          WALL THICKNESS (INCHES)                    .250
   EFFECTIVE TURNS                             3.500          CURRENT COST INDEX                      279.100
   INPUT FLOW RATE (ACFM)                 394029.950          NUMBER OF CYCLONES                         4.


                                         OUTPUT PARAMETERS FOR CYCLONE


                                         INDIVIDUAL CYCLONE PARAMETERS


   INPUT FLOW RATE (ACFM)                  98507.487          INLET VELOCITY (FT/SEC)                  96.784
   CYCLONE DIAMETER (FEET)                    11.650          CYCLONE WEIGHT (LBS)                  21228.051
   PART. SIZE (MICRONS)- 98.% EFF.            30.430          COST OF EACH CYCLONE (DOLLARS)            8154.
   PART. SIZE (MICRONS)- 50% EFF.             17.999

   TOTAL COST OF ALL CYCLONE UNITS            32614.
```

COPPER OXIDE REGENERATOR

```
                              INPUT VARIABLES FOR FAN COST

COST INDEX AS OF MAY 5,1969         279.100         TOTAL FAN CAPACITY (ACFM)          394029.950
FAN SPEED (RPM)                    1200.000         AIR DENSITY (LBS/FT**3)                  .022
OVERALL EFFICIENCY                     .850         FAN PRESSURE DROP (IN. WATER)          14.397
NUMBER OF FAN UNITS                     1.


                          FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                              INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)              394029.950         WHEEL DIAMETER (INCHES)                90.840
DRIVER BRAKE HORSEPOWER            1047.772         FAN COST (DOLLARS)                     42938.
ACTUAL DRIVER HORSEPOWER           1520.960         MOTOR COST (DOLLARS)                   16903.
FRACTIONAL CAPACITY PER FAN           1.000         EACH FAN UNIT COST (DOLLARS)           59841.

KILOWATTS REQUIRED BY DRIVER(S)     781.337         COST - ALL FAN UNITS (DOLLARS)         59841.
```

COPPER OXIDE REGENERATOR

```
                                                                           26 JUN 1969
                         SO2 REMOVAL FROM FLUE GAS
                                 CATEGORY
                            DRY METAL OXIDES
                        CAPITAL COST ESTIMATE SUMMARY
                               CASE NO. 108.

          NAME OF PROCESS                        NAME OF EQUIPMENT
              TRACOR                              REGENERATION UNIT

  FLUE GAS RATE      .1 MMSCFM
                                                            MW 1400.0
-------------------------------------------------------------------------------------

              ITEM                              COST- THOU. $        % OF TOTAL
              ----                              -------------        ----------

       1.  PURCHASED EQUIPMENT                      142.8               19.22
       2.  ERECTION LABOR                            35.7                4.80
       3.  FOUNDATION & PLATFORMS                    25.7                3.46
       4.  PIPING                                   107.1               14.41
       5.  INSTRUMENTS                               21.4                2.88
       6.  INSULATION                                11.4                1.54
       7.  ELECTRICAL                                14.3                1.92
       8.  BUILDINGS                                 35.7                4.80
       9.  LAND & YARD IMPROVEMENTS                  18.6                2.50
      10.  UTILITIES                                 57.1                7.69
      11.        PHYSICAL-PLANT COST                469.8               63.23
      12.  ENGINEERING & CONSTRUCTION                94.2               12.63

      13.        DIRECT PLANT COST                  564.0               75.92
      14.  CONTRACTOR-S FEE                          27.1                3.65
      15.  CONTINGENCY                               84.3               11.34

      16.        FIXED CAPITAL COST                 675.4               90.91
      17.  WORKING CAPITAL                           67.5                9.09

                 TOTAL INVESTMENT                   743.0              100.00
      18.  CAPITAL REQUIREMENTS
                 $/KW CAPACITY             .5
```

```
PAGE 10                         COPPER OXIDE REGENERATOR                              26 JUN 1969
                                SO2 REMOVAL FROM FLUE GAS
                                        CATEGORY
                                   DRY METAL OXIDES

                              OPERATING COST ESTIMATE SUMMARY
                           BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

                     NAME OF PROCESS                        NAME OF EQUIPMENT
                         TRACOR                              REGENERATION UNIT

            FLUE GAS RATE      .1 MMSCFM                                      MW 1400.0
                               FIXED CAPITAL COST    675428.8

-----------------------------------------------------------------------------------------

                     ITEM                                   COST- THOU. $        % OF TOTAL
                     ----                                   -------------        ----------

       1.  RAW MATERIALS & CHEMICALS                                  .0               .00
       2.  DIRECT LABOR                                               .0               .00
       3.  SUPERVISION                                                .0               .00
       4.  MAINTENANCE, 5% OF FIXED CAPITAL                         33.8              7.28
       5.  SUPPLIES, 15% OF MAINTENANCE                              5.1              1.09
       6.  UTILITIES                                                26.0              5.60
       7.  OTHER                                                   292.0             62.92
       8.       TOTAL DIRECT COST                                  356.8             76.89
       9.  PAYROLL BURDEN, 20% OF 2 & 3                               .0               .00
      10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                       19.4              4.18
      11.  PACK & SHIP                                                .0               .00
      12.  WASTE DISPOSAL                                             .0               .00
      13.  OTHER                                                      .0               .00
      14.       TOTAL INDIRECT COST                                 19.4              4.18
      15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                   67.5             14.55
      16.  TAXES, 2% OF FIXED CAPITAL                               13.5              2.91
      17.  INSURANCE, 1% OF FIXED CAPITAL                            6.8              1.46
      18.  OTHER                                                      .0               .00
      19.       TOTAL FIXED COST                                    87.8             18.92

      20.  TOTAL OPERATING COST                                    464.1            100.00
      21.  COST:  $/TON OF COAL                   .144
                  MIL/KWH                         .042
```

```
PAGE  1                           COPPER OXIDE SORBER                               26 JUN 1969

                                INPUT FOR FLUIDIZED BED


  FLOW RATE (SCFM)                        300000.000      DENSITY OF SOLID (LBS/FT**3)         100.000
  PARTICLE DIAMETER (INCHES)                   .0300      INLET CONCENT. (MOLE PERCENT)          .00300
  REACTION RATE (1/SEC)                     97.50000      OUTLET CONCENT. (MOLE PERCENT)         .00030
  RATIO- SUPERFICIAL TO MIN. VEL.              9.000      VOL. WAKE / VOL. BUBBLE                .320
  TEMPERATURE (DEG. F.)                      613.000      FRACTION OF SOLIDS IN BUBBLE           .000
  INLET PRESSURE (PSIA)                       14.700


                               OUTPUT FROM FLUIDIZED BED


  FLOW RATE (ACFM)                       1031034.200      INITIAL BUBBLE DIAMETER (FEET)         .205
  DIAMETER OF BED (FEET)                      61.082      FINAL BUBBLE DIAMETER (FEET)           .328
  HEIGHT OF BED (FEET)                         2.056      INITIAL BUBBLE VEL. (FT/SEC)          7.041
  HEIGHT OF VESSEL (FEET)                     30.541      FINIAL BUBBLE VEL. (FT/SEC)           7.523
  THICKNESS OF SHELL (INCHES)                   .312      MIN. MASS FLUX (LBS/HR-FT**2)        89.422
  BED PRESSURE DROP (IN. WATER)                3.288      MIN. FLUID VOIDAGE                     .458
  DISTR. PRESS. DROP (IN. WATER)               1.106      MIN. FLUID VEL. (FT/SEC)               .652
  TOTAL PRESS. DROP (IN. WATER)                4.333      HOLES/IN.**2 IN DISTR. PLATE          1.204
  OUTLET PRESSURE (PSIA)                      14.541      PARTICLE TERMINAL VEL. (FT/SEC)      11.835
  WEIGHT OF SORBENT (LBS)                  50210.447      SUPERFICIAL VELOCITY (FT/SEC)         5.866
  FRACTION OF SOLIDS IN CLOUD                  2.791      FRACTIONS OF BUBBLES IN BED            .846
  FRACTION OF SOLIDS IN EMULSION              -2.619
```

COPPER OXIDE SORBER

```
PAGE   3                                                                                     26 JUN 1969
                                            INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)              61.032          SHELL HEIGHT (FEET)                      30.541
  SHELL THICKNESS (INCHES)                    .312          CURRENT COST INDEX                      279.100


                                         OUTPUT PARAMETERS FOR SORBER SHELL


  WEIGHT OF SHELL (LBS)                 174267.220          LINING COST (DOLLARS)                     4282.
  WEIGHT OF HEADS (LBS)                 174267.220          COST OF VESSEL (DOLLARS)                105311.
  WEIGHT OF DISTR. PLATE (LBS)           86954.372          TOTAL COST OF SORBER (DOLLARS)          109593.
  WEIGHT OF VESSEL (LBS)                435488.830
```

COPPER OXIDE SORBER

```
PAGE  5                                                                                     26 JUN 1969
                                        INPUT PARAMETERS FOR CYCLONE


   CYCLONE REMOVAL EFFICIENCY (%)           98.000          PRESSURE DROP (INCHES WATER)          5.000
   FLUID DENSITY (LBS/FT**3)                  .038          SOLID DENSITY (LBS/FT**3)           100.000
   VISCOSITY (LBS/FT-SEC)                .00002013          WALL THICKNESS (INCHES)                .250
   EFFECTIVE TURNS                           3.500          CURRENT COST INDEX                  279.100
   INPUT FLOW RATE (ACFM)              1031034.200          NUMBER OF CYCLONES                       4.


                                        OUTPUT PARAMETERS FOR CYCLONE


                                        INDIVIDUAL CYCLONE PARAMETERS


   INPUT FLOW RATE (ACFM)               257758.550          INLET VELOCITY (FT/SEC)              73.969
   CYCLONE DIAMETER (FEET)                  21.557          CYCLONE WEIGHT (LBS)              72678.956
   PART. SIZE (MICRONS)- 98.% EFF.          39.990          COST OF EACH CYCLONE (DOLLARS)       27916.
   PART. SIZE (MICRONS)- 50% EFF.           23.654

   TOTAL COST OF ALL CYCLONE UNITS         111662.
```

COPPER OXIDE SORBER

```
                                    INPUT VARIABLES FOR FAN COST

 COST INDEX AS OF MAY 5,1969           279.100          TOTAL FAN CAPACITY (ACFM)          1031034.200
 FAN SPEED (RPM)                      1200.000          AIR DENSITY (LBS/FT**3)                   .038
 OVERALL EFFICIENCY                       .850          FAN PRESSURE DROP (IN. WATER)            9.393
 NUMBER OF FAN UNITS                        1.


                               FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                   INDIVIDUAL FAN UNIT PARAMETERS

 FAN CAPACITY (ACFM)               1031034.200          WHEEL DIAMETER (INCHES)                 73.447
 DRIVER BRAKE HORSEPOWER              1788.853          FAN COST (DOLLARS)                      24920.
 ACTUAL DRIVER HORSEPOWER             2596.723          MOTOR COST (DOLLARS)                    28096.
 FRACTIONAL CAPACITY PER FAN             1.000          EACH FAN UNIT COST (DOLLARS)            53017.


 KILOWATTS REQUIRED BY DRIVER(S)      1333.970          COST - ALL FAN UNITS (DOLLARS)          53017.
```

COPPER OXIDE SORBER

```
                                                              26 JUN 1969
                        SO2 REMOVAL FROM FLUE GAS
                                 CATEGORY
                            DRY METAL OXIDES
                      CAPITAL COST ESTIMATE SUMMARY
                               CASE NO. 105.

              NAME OF PROCESS                    NAME OF EQUIPMENT
                   TRACOR                         SORPTION UNIT

     FLUE GAS RATE     .5 MMSCFM                               MW  220.0

-----------------------------------------------------------------------------

              ITEM                               COST- THOU. $     % OF TOTAL
              ----                               -------------     ----------

     1.  PURCHASED EQUIPMENT                          274.3          19.22
     2.  ERECTION LABOR                                68.6           4.80
     3.  FOUNDATION & PLATFORMS                        49.4           3.46
     4.  PIPING                                       205.7          14.41
     5.  INSTRUMENTS                                   41.1           2.88
     6.  INSULATION                                    21.9           1.54
     7.  ELECTRICAL                                    27.4           1.92
     8.  BUILDINGS                                     68.6           4.80
     9.  LAND & YARD IMPROVEMENTS                      35.7           2.50
    10.  UTILITIES                                    109.7           7.69
    11.        PHYSICAL-PLANT COST                    902.4          63.23
    12.  ENGINEERING & CONSTRUCTION                   181.0          12.68

    13.        DIRECT PLANT COST                     1083.4          75.92
    14.  CONTRACTOR-S FEE                              52.1           3.65
    15.  CONTINGENCY                                  161.8          11.34

    16.        FIXED CAPITAL COST                    1297.3          90.91
    17.  WORKING CAPITAL                              129.7           9.09

               TOTAL INVESTMENT                      1427.0         100.00
    18.  CAPITAL REQUIREMENTS
               $/KW CAPACITY               6.5
```

COPPER OXIDE SORBER

```
                                                                                 26 JUN 1969
                        SO2 REMOVAL FROM FLUE GAS
                               CATEGORY
                           DRY METAL OXIDES

                      OPERATING COST ESTIMATE SUMMARY
                    BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

           NAME OF PROCESS                          NAME OF EQUIPMENT
               TRACOR                                 SORPTION UNIT

    FLUE GAS RATE     .5 MMSCFM                                         MW  220.0
                          FIXED CAPITAL COST   1297305.9

------------------------------------------------------------------------------------------

                  ITEM                                  COST- THOU. $      % OF TOTAL
                  ----                                  -------------      ----------

     1.  RAW MATERIALS & CHEMICALS                               126.0           23.40
     2.  DIRECT LABOR                                             54.0           10.03
     3.  SUPERVISION                                              27.4            5.09
     4.  MAINTENANCE, 5% OF FIXED CAPITAL                         64.9           12.05
     5.  SUPPLIES, 15% OF MAINTENANCE                              9.7            1.81
     6.  UTILITIES                                                44.4            8.25
     7.  OTHER                                                   -50.9           -9.45
     8.        TOTAL DIRECT COST                                 275.5           51.17
     9.  PAYROLL BURDEN, 20% OF 2 & 3                             16.3            3.02
    10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                       78.0           14.49
    11.  PACK & SHIP                                                .0             .00
    12.  WASTE DISPOSAL                                             .0             .00
    13.  OTHER                                                      .0             .00
    14.        TOTAL INDIRECT COST                                94.3           17.51
    15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                  129.7           24.09
    16.  TAXES, 2% OF FIXED CAPITAL                               25.9            4.82
    17.  INSURANCE, 1% OF FIXED CAPITAL                           13.0            2.41
    18.  OTHER                                                      .0             .00
    19.        TOTAL FIXED COST                                  168.6           31.32

    20.  TOTAL OPERATING COST                                    538.4          100.00
    21.  COST:  $/TON OF COAL                   1.079
                MIL/KWH                          .309
```

```
PAGE  1                              COPPER OXIDE REGENERATOR                                   26 JUN 1969

                                     INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                        21152.000        DENSITY OF SOLID (LBS/FT**3)               100.000
PARTICLE DIAMETER (INCHES)                  .0300        INLET CONCENT. (MOLE PERCENT)             10.00000
REACTION RATE (1/SEC)                    10.00000        OUTLET CONCENT. (MOLE PERCENT)             1.00000
RATIO- SUPERFICIAL TO MIN. VEL.             9.000        VOL. WAKE / VOL. BUBBLE                       .320
TEMPERATURE (DEG. F.)                    1377.000        FRACTION OF SOLIDS IN BUBBLE                  .000
INLET PRESSURE (PSIA)                      14.700


                                     OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                        74682.091        INITIAL BUBBLE DIAMETER (FEET)                .229
DIAMETER OF BED (FEET)                     18.763        FINAL BUBBLE DIAMETER (FEET)                  .328
HEIGHT OF BED (FEET)                        2.948        INITIAL BUBBLE VEL. (FT/SEC)                 5.928
HEIGHT OF VESSEL (FEET)                     9.384        FINIAL BUBBLE VEL. (FT/SEC)                  6.310
THICKNESS OF SHELL (INCHES)                  .250        MIN. MASS FLUX (LBS/HR-FT**2)               40.074
BED PRESSURE DROP (IN. WATER)               7.036        MIN. FLUID VOIDAGE                            .465
DISTR. PRESS. DROP (IN. WATER)              2.361        MIN. FLUID VEL. (FT/SEC)                      .500
TOTAL PRESS. DROP (IN. WATER)               9.337        HOLES/IN.**2 IN DISTR. PLATE                  .483
OUTLET PRESSURE (PSIA)                     14.361        PARTICLE TERMINAL VEL. (FT/SEC)             14.207
WEIGHT OF SORBENT (LBS)                 10144.842        SUPERFICIAL VELOCITY (FT/SEC)                4.500
FRACTION OF SOLIDS IN CLOUD                 1.567        FRACTIONS OF BUBBLES IN BED                   .767
FRACTION OF SOLIDS IN EMULSION             -1.326
```

```
PAGE  3                          COPPER OXIDE REGENERATOR                                        26 JUN 1969
                                     INPUT PARAMETERS

  INSIDE SHELL DIAMETER (FEET)             18.768          SHELL HEIGHT (FEET)                        9.384
  SHELL THICKNESS (INCHES)                   .250          CURRENT COST INDEX                       279.100


                                 OUTPUT PARAMETERS FOR SORBER SHELL


  WEIGHT OF SHELL (LBS)                 13174.596          LINING COST (DOLLARS)                       404.
  WEIGHT OF HEADS (LBS)                 13174.596          COST OF VESSEL (DOLLARS)                  10627.
  WEIGHT OF DISTR. PLATE (LBS)           8209.420          TOTAL COST OF SORBER (DOLLARS)            11031.
  WEIGHT OF VESSEL (LBS)                34558.611
```

COPPER OXIDE REGENERATOR

```
PAGE 3                                                                           26 JUN 1969
                                          INPUT PARAMETERS FOR CYCLONE

 CYCLONE REMOVAL EFFICIENCY (%)         98.000           PRESSURE DROP (INCHES WATER)               5.000
 FLUID DENSITY (LBS/FT**3)                .022           SOLID DENSITY (LBS/FT**3)                100.000
 VISCOSITY (LBS/FT-SEC)              .00002830           WALL THICKNESS (INCHES)                     .250
 EFFECTIVE TURNS                         3.500           CURRENT COST INDEX                       279.100
 INPUT FLOW RATE (ACFM)              74682.091           NUMBER OF CYCLONES                            4.


                                          OUTPUT PARAMETERS FOR CYCLONE


                                         INDIVIDUAL CYCLONE PARAMETERS


 INPUT FLOW RATE (ACFM)              18670.522           INLET VELOCITY (FT/SEC)                   96.784
 CYCLONE DIAMETER (FEET)                 5.072           CYCLONE WEIGHT (LBS)                    4023.438
 PART. SIZE (MICRONS)- 98.% EFF.        20.078           COST OF EACH CYCLONE (DOLLARS)              1545.
 PART. SIZE (MICRONS)- 50% EFF.         11.876

 TOTAL COST OF ALL CYCLONE UNITS          6182.
```

```
                              INPUT VARIABLES FOR FAN COST


COST INDEX AS OF MAY 5,1969        279.100      TOTAL FAN CAPACITY (ACFM)          74682.091
FAN SPEED (RPM)                   1200.000      AIR DENSITY (LBS/FT**3)                 .022
OVERALL EFFICIENCY                    .850      FAN PRESSURE DROP (IN. WATER)         14.397
NUMBER OF FAN UNITS                    1.


                         FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                              INDIVIDUAL FAN UNIT PARAMETERS


FAN CAPACITY (ACFM)              74682.090      WHEEL DIAMETER (INCHES)               75.401
DRIVER BRAKE HORSEPOWER            198.589      FAN COST (DOLLARS)                    26653.
ACTUAL DRIVER HORSEPOWER           288.274      MOTOR COST (DOLLARS)                   3481.
FRACTIONAL CAPACITY PER FAN          1.000      EACH FAN UNIT COST (DOLLARS)          30134.

KILOWATTS REQUIRED BY DRIVER(S)    148.090      COST - ALL FAN UNITS (DOLLARS)        30134.
```

COPPER OXIDE REGENERATOR

```
                    SO2 REMOVAL FROM FLUE GAS
                           CATEGORY
                       DRY METAL OXIDES
                  CAPITAL COST ESTIMATE SUMMARY
                          CASE NO. 199.

        NAME OF PROCESS                   NAME OF EQUIPMENT
            TRACOR                         REGENERATION UNIT

  FLUE GAS RATE     .0 MMSCFM                              MW  220.0

--------------------------------------------------------------------------------------------

                ITEM                                  COST- THOU. $        % OF TOTAL
                ----                                  -------------        ----------

  1.   PURCHASED EQUIPMENT                                  47.3              19.22
  2.   ERECTION LABOR                                       11.8               4.80
  3.   FOUNDATION & PLATFORMS                                8.5               3.46
  4.   PIPING                                               35.5              14.41
  5.   INSTRUMENTS                                           7.1               2.88
  6.   INSULATION                                            3.8               1.54
  7.   ELECTRICAL                                            4.7               1.92
  8.   BUILDINGS                                            11.8               4.80
  9.   LAND & YARD IMPROVEMENTS                              6.2               2.50
 10.   UTILITIES                                            18.9               7.69
 11.         PHYSICAL-PLANT COST                           155.8              63.23
 12.   ENGINEERING & CONSTRUCTION                           31.2              12.68

 13.         DIRECT PLANT COST                             187.0              75.92
 14.   CONTRACTOR-S FEE                                      9.0               3.65
 15.   CONTINGENCY                                          27.9              11.34

 16.         FIXED CAPITAL COST                            224.0              90.91
 17.   WORKING CAPITAL                                      22.4               9.09

             TOTAL INVESTMENT                              246.3             100.00
 18.   CAPITAL REQUIREMENTS
             $/KW CAPACITY                    1.1
```

```
                         COPPER OXIDE REGENERATOR                                  26 JUN 1969
                          SO2 REMOVAL FROM FLUE GAS
                                  CATEGORY
                              DRY METAL OXIDES

                       OPERATING COST ESTIMATE SUMMARY
                    BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

            NAME OF PROCESS                            NAME OF EQUIPMENT
                TRACOR                                  REGENERATION UNIT

   FLUE GAS RATE      .0 MMSCFM                                        MW  220.0
                       FIXED CAPITAL COST    223951.2

-------------------------------------------------------------------------------------------

                  ITEM                                 COST- THOU. $         % OF TOTAL
                  ----                                 -------------         ----------

      1.  RAW MATERIALS & CHEMICALS                               .0                .00
      2.  DIRECT LABOR                                            .0                .00
      3.  SUPERVISION                                             .0                .00
      4.  MAINTENANCE, 5% OF FIXED CAPITAL                      11.2              10.28
      5.  SUPPLIES, 15% OF MAINTENANCE                           1.7               1.54
      6.  UTILITIES                                              4.9               4.52
      7.  OTHER                                                 55.6              51.03
      8.        TOTAL DIRECT COST                               73.4              67.37
      9.  PAYROLL BURDEN, 20% OF 2 & 3                            .0                .00
     10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                     6.4               5.91
     11.  PACK & SHIP                                             .0                .00
     12.  WASTE DISPOSAL                                          .0                .00
     13.  OTHER                                                   .0                .00
     14.        TOTAL INDIRECT COST                              6.4               5.91
     15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                22.4              20.55
     16.  TAXES, 2% OF FIXED CAPITAL                             4.5               4.11
     17.  INSURANCE, 1% OF FIXED CAPITAL                         2.2               2.06
     18.  OTHER                                                   .0                .00
     19.        TOTAL FIXED COST                                29.1              26.72

     20.  TOTAL OPERATING COST                                 109.0             100.00
     21.  COST:  $/TON OF COAL                 .218
                 MIL/KWH                       .067
```

```
PAGE  1                                                                                        26 JUN 1969
                                          COPPER OXIDE SORBER
                                         INPUT FOR FLUIDIZED BED

   FLOW RATE (SCFM)                      20000.000          DENSITY OF SOLID (LBS/FT**3)             100.000
   PARTICLE DIAMETER (INCHES)                .0300          INLET CONCENT. (MOLE PERCENT)             .02900
   REACTION RATE (1/SEC)                  97.50000          OUTLET CONCENT. (MOLE PERCENT)            .00500
   RATIO- SUPERFICIAL TO MIN. VEL.           9.000          VOL. WAKE / VOL. BUBBLE                     .320
   TEMPERATURE (DEG. F.)                   613.000          FRACTION OF SOLIDS IN BUBBLE                .000
   INLET PRESSURE (PSIA)                    14.700


                                        OUTPUT FROM FLUIDIZED BED

   FLOW RATE (ACFM)                      41241.358          INITIAL BUBBLE DIAMETER (FEET)              .205
   DIAMETER OF BED (FEET)                   12.216          FINAL BUBBLE DIAMETER (FEET)                .328
   HEIGHT OF BED (FEET)                      1.569          INITIAL BUBBLE VEL. (FT/SEC)               7.041
   HEIGHT OF VESSEL (FEET)                   6.108          FINIAL BUBBLE VEL. (FT/SEC)                7.523
   THICKNESS OF SHELL (INCHES)                .250          MIN. MASS FLUX (LBS/HR-FT**2)             89.422
   BED PRESSURE DROP (IN. WATER)             2.506          MIN. FLUID VOIDAGE                          .458
   DISTR. PRESS. DROP (IN. WATER)             .843          MIN. FLUID VEL. (FT/SEC)                    .652
   TOTAL PRESS. DROP (IN. WATER)             3.349          HOLES/IN.**2 IN DISTR. PLATE               1.379
   OUTLET PRESSURE (PSIA)                   14.579          PARTICLE TERMINAL VEL. (FT/SEC)           11.835
   WEIGHT OF SORBENT (LBS)                1531.088          SUPERFICIAL VELOCITY (FT/SEC)              5.866
   FRACTION OF SOLIDS IN CLOUD               2.791          FRACTIONS OF BUBBLES IN BED                 .846
   FRACTION OF SOLIDS IN EMULSION           -2.619
```

```
PAGE  3                              COPPER OXIDE SORBER                                     26 JUN 1969
                                   INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)             12.215          SHELL HEIGHT (FEET)                     6.108
  SHELL THICKNESS (INCHES)                   .250          CURRENT COST INDEX                    279.100


                                 OUTPUT PARAMETERS FOR SORBER SHELL


  WEIGHT OF SHELL (LBS)                  5581.825          LINING COST (DOLLARS)                   171.
  WEIGHT OF HEADS (LBS)                  5581.825          COST OF VESSEL (DOLLARS)               4828.
  WEIGHT OF DISTR. PLATE (LBS)           3479.175          TOTAL COST OF SORBER (DOLLARS)         5000.
  WEIGHT OF VESSEL (LBS)                14641.826
```

COPPER OXIDE SORBER

```
PAGE  5                                                                        25 JUN 1969
                                   INPUT PARAMETERS FOR CYCLONE

CYCLONE REMOVAL EFFICIENCY (%)          98.000          PRESSURE DROP (INCHES WATER)          5.000
FLUID DENSITY (LBS/FT**3)                 .038          SOLID DENSITY (LBS/FT**3)           100.000
VISCOSITY (LBS/FT-SEC)               .00002018          WALL THICKNESS (INCHES)                .250
EFFECTIVE TURNS                          3.500          CURRENT COST INDEX                  279.100
INPUT FLOW RATE (ACFM)               41241.363          NUMBER OF CYCLONES                       2.


                                   OUTPUT PARAMETERS FOR CYCLONE


                                  INDIVIDUAL CYCLONE PARAMETERS


INPUT FLOW RATE (ACFM)               20620.684          INLET VELOCITY (FT/SEC)              73.969
CYCLONE DIAMETER (FEET)                  6.097          CYCLONE WEIGHT (LBS)               5814.317
PART. SIZE (MICRONS)- 98.0 EFF.         21.263          COST OF EACH CYCLONE (DOLLARS)        2233.
PART. SIZE (MICRONS)- 50% EFF.          12.580

TOTAL COST OF ALL CYCLONE UNITS          4466.
```

```
PAGE  7                                                                         26 JUN 1969
```

COPPER OXIDE SORBER

```
                              INPUT VARIABLES FOR FAN COST

    COST INDEX AS OF MAY 5,1969         279.100      TOTAL FAN CAPACITY (ACFM)         41241.368
    FAN SPEED (RPM)                    1200.000      AIR DENSITY (LBS/FT**3)                .038
    OVERALL EFFICIENCY                     .850      FAN PRESSURE DROP (IN. WATER)         8.349
    NUMBER OF FAN UNITS                      1.


                          FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                              INDIVIDUAL FAN UNIT PARAMETERS

    FAN CAPACITY (ACFM)               41241.368      WHEEL DIAMETER (INCHES)              49.251
    DRIVER BRAKE HORSEPOWER              63.600      FAN COST (DOLLARS)                    8958.
    ACTUAL DRIVER HORSEPOWER             92.322      MOTOR COST (DOLLARS)                  1180.
    FRACTIONAL CAPACITY PER FAN           1.000      EACH FAN UNIT COST (DOLLARS)         10139.

    KILOWATTS REQUIRED BY DRIVER(S)      47.427      COST - ALL FAN UNITS (DOLLARS)       10139.
```

COPPER OXIDE SORBER

```
                          SO2 REMOVAL FROM FLUE GAS
                                  CATEGORY
                              DRY METAL OXIDES
                        CAPITAL COST ESTIMATE SUMMARY
                                CASE NO. 107.

              NAME OF PROCESS                        NAME OF EQUIPMENT
                  TRACOR                               SORPTION UNIT

     FLUE GAS RATE     .0 MMSCFM                                    MW   13.8

-------------------------------------------------------------------------------------

              ITEM                                   COST- THOU. $        % OF TOTAL
              ----                                   -------------        ----------

     1.  PURCHASED EQUIPMENT                                 19.6              19.22
     2.  ERECTION LABOR                                       4.9               4.80
     3.  FOUNDATION & PLATFORMS                               3.5               3.46
     4.  PIPING                                              14.7              14.41
     5.  INSTRUMENTS                                          2.9               2.88
     6.  INSULATION                                           1.6               1.54
     7.  ELECTRICAL                                           2.0               1.92
     8.  BUILDINGS                                            4.9               4.80
     9.  LAND & YARD IMPROVEMENTS                             2.5               2.50
    10.  UTILITIES                                            7.8               7.69
    11.        PHYSICAL-PLANT COST                           64.5              63.23
    12.  ENGINEERING & CONSTRUCTION                          12.9              12.68

    13.        DIRECT PLANT COST                             77.4              75.92
    14.  CONTRACTOR-S FEE                                     3.7               3.65
    15.  CONTINGENCY                                         11.6              11.34

    16.        FIXED CAPITAL COST                            92.7              90.91
    17.  WORKING CAPITAL                                      9.3               9.09

               TOTAL INVESTMENT                             102.0             100.00
    18.  CAPITAL REQUIREMENTS
               $/KW CAPACITY                     7.4
```

```
                                   COPPER OXIDE SORBER                              26 JUN 1969
                                SO2 REMOVAL FROM FLUE GAS
                                        CATEGORY
                                    DRY METAL OXIDES

                            OPERATING COST ESTIMATE SUMMARY
                          BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

                     NAME OF PROCESS                       NAME OF EQUIPMENT
                        TRACOR                               SORPTION UNIT

         FLUE GAS RATE      .0 MMSCFM                                      MW   13.8
                                 FIXED CAPITAL COST      92731.0
------------------------------------------------------------------------------------------

                       ITEM                                    COST- THOU. $       % OF TOTAL
                       ----                                    -------------       ----------

     1.  RAW MATERIALS & CHEMICALS                                  47.1              25.03
     2.  DIRECT LABOR                                               54.0              28.71
     3.  SUPERVISION                                                27.4              14.57
     4.  MAINTENANCE, 5% OF FIXED CAPITAL                            4.6               2.47
     5.  SUPPLIES, 15% OF MAINTENANCE                                 .7                .37
     6.  UTILITIES                                                   1.6                .84
     7.  OTHER                                                     -19.0             -10.10
     8.       TOTAL DIRECT COST                                    116.4              61.88
     9.  PAYROLL BURDEN, 20% OF 2 & 3                               16.3               8.66
    10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                         43.4              23.06
    11.  PACK & SHIP                                                  .0                .00
    12.  WASTE DISPOSAL                                               .0                .00
    13.  OTHER                                                        .0                .00
    14.       TOTAL INDIRECT COST                                   59.6              31.71
    15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                      9.3               4.93
    16.  TAXES, 2% OF FIXED CAPITAL                                  1.9                .99
    17.  INSURANCE, 1% OF FIXED CAPITAL                               .9                .49
    18.  OTHER                                                        .0                .00
    19.       TOTAL FIXED COST                                      12.1               6.41

    20.  TOTAL OPERATING COST                                      188.1             100.00
    21.  COST:   $/TON OF COAL                   6.075
                 MIL/KWH                         1.717
```

```
PAGE  1                                   COPPER OXIDE REGENERATOR                                   26 JUN 1969

                                          INPUT FOR FLUIDIZED BED


 FLOW RATE (SCFM)                             7577.000          DENSITY OF SOLID (LBS/FT**3)              100.000
 PARTICLE DIAMETER (INCHES)                     .0300           INLET CONCENT. (MOLE PERCENT)            10.00000
 REACTION RATE (1/SEC)                        10.00000          OUTLET CONCENT. (MOLE PERCENT)            1.00000
 RATIO- SUPERFICIAL TO MIN. VEL.                 9.000          VOL. WAKE / VOL. BUBBLE                      .320
 TEMPERATURE (DEG. F.)                        1377.000          FRACTION OF SOLIDS IN BUBBLE                 .000
 INLET PRESSURE (PSIA)                          14.700


                                          OUTPUT FROM FLUIDIZED BED


 FLOW RATE (ACFM)                            26752.374          INITIAL BUBBLE DIAMETER (FEET)               .229
 DIAMETER OF BED (FEET)                         11.233          FINAL BUBBLE DIAMETER (FEET)                 .328
 HEIGHT OF BED (FEET)                            2.948          INITIAL BUBBLE VEL. (FT/SEC)                5.928
 HEIGHT OF VESSEL (FEET)                         5.616          FINIAL BUBBLE VEL. (FT/SEC)                 6.310
 THICKNESS OF SHELL (INCHES)                      .250          MIN. MASS FLUX (LBS/HR-FT**2)              40.074
 BED PRESSURE DROP (IN. WATER)                   7.036          MIN. FLUID VOIDAGE                           .465
 DISTR. PRESS. DROP (IN. WATER)                  2.361          MIN. FLUID VEL. (FT/SEC)                     .500
 TOTAL PRESS. DROP (IN. WATER)                   9.397          HOLES/IN.**2 IN DISTR. PLATE                 .483
 OUTLET PRESSURE (PSIA)                         14.361          PARTICLE TERMINAL VEL. (FT/SEC)            14.207
 WEIGHT OF SORBENT (LBS)                      3634.052          SUPERFICIAL VELOCITY (FT/SEC)               4.500
 FRACTION OF SOLIDS IN CLOUD                     1.567          FRACTIONS OF BUBBLES IN BED                  .767
 FRACTION OF SOLIDS IN EMULSION                 -1.326
```

COPPER OXIDE REGENERATOR

```
PAGE  3                                                                                  26 JUN 1969
                                         INPUT PARAMETERS FOR SORBER

   INSIDE SHELL DIAMETER (FEET)             11.233          SHELL HEIGHT (FEET)                      5.616
   SHELL THICKNESS (INCHES)                   .250          CURRENT COST INDEX                     279.100


                                        OUTPUT PARAMETERS FOR SORBER SHELL

   WEIGHT OF SHELL (LBS)                  4719.360          LINING COST (DOLLARS)                    145.
   WEIGHT OF HEADS (LBS)                  4719.360          COST OF VESSEL (DOLLARS)                4136.
   WEIGHT OF DISTR. PLATE (LBS)           2940.751          TOTAL COST OF SORBER (DOLLARS)          4281.
   WEIGHT OF VESSEL (LBS)                12379.472
```

```
PAGE  5                                    COPPER OXIDE REGENERATOR                                   26 JUN 1969
                                           INPUT PARAMETERS FOR CYCLONE

    CYCLONE REMOVAL EFFICIENCY (%)          98.000          PRESSURE DROP (INCHES WATER)            5.000
    FLUID DENSITY (LBS/FT**3)                 .022          SOLID DENSITY (LBS/FT**3)             100.000
    VISCOSITY (LBS/FT-SEC)               .00002830          WALL THICKNESS (INCHES)                  .250
    EFFECTIVE TURNS                          3.500          CURRENT COST INDEX                    273.100
    INPUT FLOW RATE (ACFM)               28752.374          NUMBER OF CYCLONES                         2.


                                           OUTPUT PARAMETERS FOR CYCLONE


                                          INDIVIDUAL CYCLONE PARAMETERS


    INPUT FLOW RATE (ACFM)               13376.187          INLET VELOCITY (FT/SEC)                96.784
    CYCLONE DIAMETER (FEET)                  4.293          CYCLONE WEIGHT (LBS)                 2882.526
    PART. SIZE (MICRONS)- 98.% EFF.         18.472          COST OF EACH CYCLONE (DOLLARS)          1107.
    PART. SIZE (MICRONS)- 50% EFF.          10.926

    TOTAL COST OF ALL CYCLONE UNITS          2214.
```

```
PAGE  7                       COPPER OXIDE REGENERATOR                              26 JUN 1969

                               INPUT VARIABLES FOR FAN COST

  COST INDEX AS OF MAY 5,1969          279.100        TOTAL FAN CAPACITY (ACFM)             26752.374
  FAN SPEED (RPM)                     1200.000        AIR DENSITY (LBS/FT**3)                    .022
  OVERALL EFFICIENCY                      .850        FAN PRESSURE DROP (IN. WATER)            14.397
  NUMBER OF FAN UNITS                      1.


                           FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                               INDIVIDUAL FAN UNIT PARAMETERS

  FAN CAPACITY (ACFM)                26752.374        WHEEL DIAMETER (INCHES)                  67.212
  DRIVER BRAKE HORSEPOWER               71.138        FAN COST (DOLLARS)                       19857.
  ACTUAL DRIVER HORSEPOWER             103.264        MOTOR COST (DOLLARS)                      1313.
  FRACTIONAL CAPACITY PER FAN            1.000        EACH FAN UNIT COST (DOLLARS)             21170.

  KILOWATTS REQUIRED BY DRIVER(S)       53.048        COST - ALL FAN UNITS (DOLLARS)           21170.
```

COPPER OXIDE REGENERATOR

```
PAGE  9                                                                     26 JUN 1969
                              SO2 REMOVAL FROM FLUE GAS
                                      CATEGORY
                                 DRY METAL OXIDES
                             CAPITAL COST ESTIMATE SUMMARY
                                    CASE NO. 193.

                   NAME OF PROCESS                      NAME OF EQUIPMENT
                       TRACOR                            REGENERATION UNIT

         FLUE GAS RATE      .0 MMSCFM                                      MW    13.8

-------------------------------------------------------------------------------------

                      ITEM                                COST- THOU. $      % OF TOTAL
                      ----                                -------------      ----------

         1.  PURCHASED EQUIPMENT                                  27.7           19.22
         2.  ERECTION LABOR                                        6.9            4.80
         3.  FOUNDATION & PLATFORMS                                5.0            3.46
         4.  PIPING                                               20.7           14.41
         5.  INSTRUMENTS                                           4.1            2.88
         6.  INSULATION                                            2.2            1.54
         7.  ELECTRICAL                                            2.8            1.92
         8.  BUILDINGS                                             6.9            4.80
         9.  LAND & YARD IMPROVEMENTS                              3.6            2.50
        10.  UTILITIES                                            11.1            7.69
        11.        PHYSICAL-PLANT COST                            91.0           63.23
        12.  ENGINEERING & CONSTRUCTION                           18.3           12.68

        13.        DIRECT PLANT COST                             109.3           75.92
        14.  CONTRACTOR-S FEE                                      5.3            3.65
        15.  CONTINGENCY                                          16.3           11.34

        16.        FIXED CAPITAL COST                            130.9           90.91
        17.  WORKING CAPITAL                                      13.1            9.09

                   TOTAL INVESTMENT                              143.9          100.00
        18.  CAPITAL REQUIREMENTS
                   $/KW CAPACITY                 10.4
```

COPPER OXIDE REGENERATOR

```
                            SO2 REMOVAL FROM FLUE GAS
                                    CATEGORY
                                DRY METAL OXIDES

                        OPERATING COST ESTIMATE SUMMARY
                     BASIS:  330 DAY/YEAR &   70.0 % CAPACITY

           NAME OF PROCESS                          NAME OF EQUIPMENT
               TRACOR                                REGENERATION UNIT

 FLUE GAS RATE      .0 MMSCFM                                      MW   13.8
                         FIXED CAPITAL COST    130854.6

------------------------------------------------------------------------------------------

               ITEM                                    COST- THOU. $        % OF TOTAL
               ----                                    -------------        ----------

   1.  RAW MATERIALS & CHEMICALS                                 .0               .00
   2.  DIRECT LABOR                                              .0               .00
   3.  SUPERVISION                                               .0               .00
   4.  MAINTENANCE, 5% OF FIXED CAPITAL                         6.5             13.03
   5.  SUPPLIES, 15% OF MAINTENANCE                             1.0              1.96
   6.  UTILITIES                                                1.8              3.53
   7.  OTHER                                                   19.9             39.87
   8.        TOTAL DIRECT COST                                 29.2             58.45
   9.  PAYROLL BURDEN, 20% OF 2 & 3                              .0               .00
  10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                       3.8              7.53
  11.  PACK & SHIP                                               .0               .00
  12.  WASTE DISPOSAL                                            .0               .00
  13.  OTHER                                                     .0               .00
  14.        TOTAL INDIRECT COST                                3.8              7.53
  15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                  13.1             26.17
  16.  TAXES, 2% OF FIXED CAPITAL                               2.6              5.23
  17.  INSURANCE, 1% OF FIXED CAPITAL                           1.3              2.62
  18.  OTHER                                                     .0               .00
  19.        TOTAL FIXED COST                                  17.0             34.03

  20.  TOTAL OPERATING COST                                    50.0            100.00
  21.  COST:  $/TON OF COAL                 1.615
              MIL/KWH                        .456
```

```
                                      IRON OXIDE SORBER                                   26 JUN 1969

                                  INPUT FOR FLUIDIZED BED


FLOW RATE (SCFM)                      2500000.000      DENSITY OF SOLID (LBS/FT**3)           100.000
PARTICLE DIAMETER (INCHES)                 .0300       INLET CONCENT. (MOLE PERCENT)           .00300
REACTION RATE (1/SEC)                   68.00000       OUTLET CONCENT. (MOLE PERCENT)          .00015
RATIO- SUPERFICIAL TO MIN. VEL.            9.000       VOL. WAKE / VOL. BUBBLE                   .320
TEMPERATURE (DEG. F.)                    648.000       FRACTION OF SOLIDS IN BUBBLE              .000
INLET PRESSURE (PSIA)                     14.700


                                  OUTPUT FROM FLUIDIZED BED


FLOW RATE (ACFM)                      5323375.500      INITIAL BUBBLE DIAMETER (FEET)            .207
DIAMETER OF BED (FEET)                   133.954       FINAL BUBBLE DIAMETER (FEET)              .328
HEIGHT OF BED (FEET)                       2.167       INITIAL BUBBLE VEL. (FT/SEC)             6.961
HEIGHT OF VESSEL (FEET)                   69.977       FINIAL BUBBLE VEL. (FT/SEC)              7.437
THICKNESS OF SHELL (INCHES)                 .436       MIN. MASS FLUX (LBS/HR-FT**2)           85.167
BED PRESSURE DROP (IN. WATER)              3.007       MIN. FLUID VOIDAGE                        .458
DISTR. PRESS. DROP (IN. WATER)             1.019       MIN. FLUID VEL. (FT/SEC)                  .641
TOTAL PRESS. DROP (IN. WATER)              4.026       HOLES/IN.**2 IN DISTR. PLATE             1.214
OUTLET PRESSURE (PSIA)                    14.555       PARTICLE TERMINAL VEL. (FT/SEC)         11.963
WEIGHT OF SORBENT (LBS)               241086.127       SUPERFICIAL VELOCITY (FT/SEC)            5.769
FRACTION OF SOLIDS IN CLOUD                2.672       FRACTIONS OF BUBBLES IN BED               .866
FRACTION OF SOLIDS IN EMULSION            -2.496
```

IRON OXIDE SORBER

```
PAGE   3                                                                                  26 JUN 1969
                                          INPUT PARAMETERS FOR SORBER

   INSIDE SHELL DIAMETER (FEET)             139.954          SHELL HEIGHT (FEET)                    69.977
   SHELL THICKNESS (INCHES)                    .435          CURRENT COST INDEX                    279.100

                                        OUTPUT PARAMETERS FOR SORBER SHELL

   WEIGHT OF SHELL (LBS)                1276750.300          LINING COST (DOLLARS)                  22480.
   WEIGHT OF HEADS (LBS)                1276750.300          COST OF VESSEL (DOLLARS)              577046.
   WEIGHT OF DISTR. PLATE (LBS)          456500.000          TOTAL COST OF SORBER (DOLLARS)        599525.
   WEIGHT OF VESSEL (LBS)               3010000.700
```

```
                                        IRON OXIDE SORBER
                                                                                      26 JUN 1969
                                   INPUT PARAMETERS FOR CYCLONE

   CYCLONE REMOVAL EFFICIENCY (%)          98.000          PRESSURE DROP (INCHES WATER)          5.000
   FLUID DENSITY (LBS/FT**3)                 .037          SOLID DENSITY (LBS/FT**3)           100.000
   VISCOSITY (LBS/FT-SEC)               .00002061          WALL THICKNESS (INCHES)                .250
   EFFECTIVE TURNS                          3.500          CURRENT COST INDEX                  279.100
   INPUT FLOW RATE (ACFM)             5323375.500          NUMBER OF CYCLONES                       4.


                                   OUTPUT PARAMETERS FOR CYCLONE


                                  INDIVIDUAL CYCLONE PARAMETERS

   INPUT FLOW RATE (ACFM)             1330843.900          INLET VELOCITY (FT/SEC)              75.166
   CYCLONE DIAMETER (FEET)                 48.591          CYCLONE WEIGHT (LBS)             369277.390
   PART. SIZE (MICRONS)- 98.% EFF.         60.193          COST OF EACH CYCLONE (DOLLARS)     141838.
   PART. SIZE (MICRONS)- 50% EFF.          35.603


   TOTAL COST OF ALL CYCLONE UNITS        567350.
```

```
                                    INPUT VARIABLES FOR FAN COST

   COST INDEX AS OF MAY 5,1969          279.100        TOTAL FAN CAPACITY (ACFM)         5323375.500
   FAN SPEED (RPM)                     1200.000        AIR DENSITY (LBS/FT**3)                  .037
   OVERALL EFFICIENCY                      .350        FAN PRESSURE DROP (IN. WATER)           9.026
   NUMBER OF FAN UNITS                       1.


                                 FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                     INDIVIDUAL FAN UNIT PARAMETERS


   FAN CAPACITY (ACFM)              5323375.400        WHEEL DIAMETER (INCHES)                88.044
   DRIVER BRAKE HORSEPOWER             8875.034        FAN COST (DOLLARS)                     39636.
   ACTUAL DRIVER HORSEPOWER           12333.113        MOTOR COST (DOLLARS)                  128667.
   FRACTIONAL CAPACITY PER FAN            1.000        EACH FAN UNIT COST (DOLLARS)          168302.

   KILOWATTS REQUIRED BY DRIVER(S)     6618.221        COST - ALL FAN UNITS (DOLLARS)        168302.
```

IRON OXIDE SORBER

```
                                                                        26 JUN 1969
                          SO2 REMOVAL FROM FLUE GAS
                                  CATEGORY
                             DRY METAL OXIDES
                        CAPITAL COST ESTIMATE SUMMARY
                               CASE NO. 104.

           NAME OF PROCESS                     NAME OF EQUIPMENT
               TRACOR                           SORPTION UNIT

   FLUE GAS RATE    2.5 MMSCFM                                  MW 1400.0

------------------------------------------------------------------------------------

                ITEM                            COST- THOU. $       % OF TOTAL
                ----                            -------------       ----------

   1.  PURCHASED EQUIPMENT                          1335.2             19.22
   2.  ERECTION LABOR                                333.8              4.80
   3.  FOUNDATION & PLATFORMS                        240.3              3.46
   4.  PIPING                                       1001.4             14.41
   5.  INSTRUMENTS                                   200.3              2.88
   6.  INSULATION                                    106.8              1.54
   7.  ELECTRICAL                                    133.5              1.92
   8.  BUILDINGS                                     333.8              4.80
   9.  LAND & YARD IMPROVEMENTS                      173.6              2.50
  10.  UTILITIES                                     534.1              7.69
  11.        PHYSICAL-PLANT COST                    4392.7             63.23
  12.  ENGINEERING & CONSTRUCTION                    881.2             12.68

  13.        DIRECT PLANT COST                      5274.0             75.92
  14.  CONTRACTOR-S FEE                              253.7              3.65
  15.  CONTINGENCY                                   787.8             11.34

  16.        FIXED CAPITAL COST                     6315.4             90.91
  17.  WORKING CAPITAL                               631.5              9.09

             TOTAL INVESTMENT                       6946.9            100.00
  18.  CAPITAL REQUIREMENTS
             $/KW CAPACITY               5.0
```

IRON OXIDE SORBER

```
                                                                          25 JUN 1969
                              SO2 REMOVAL FROM FLUE GAS
                                      CATEGORY
                                 DRY METAL OXIDES

                            OPERATING COST ESTIMATE SUMMARY
                         BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

                  NAME OF PROCESS                       NAME OF EQUIPMENT
                      TRACOR                             SORPTION UNIT

       FLUE GAS RATE     2.5 MMSCFM                                  MW 1400.0
                              FIXED CAPITAL COST    6315389.9

---------------------------------------------------------------------------------------

                  ITEM                                    COST- THOU. $        % OF TOTAL
                  ----                                    -------------        ----------

   1.  RAW MATERIALS & CHEMICALS                                  660.5             30.72
   2.  DIRECT LABOR                                                54.0              2.51
   3.  SUPERVISION                                                 27.4              1.27
   4.  MAINTENANCE, 5% OF FIXED CAPITAL                           315.8             14.69
   5.  SUPPLIES, 15% OF MAINTENANCE                                47.4              2.20
   6.  UTILITIES                                                  220.3             10.25
   7.  OTHER                                                     -234.9            -10.92
   8.        TOTAL DIRECT COST                                   1090.4             50.72
   9.  PAYROLL BURDEN, 20% OF 2 & 3                                16.3               .76
  10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                         222.3             10.34
  11.  PACK & SHIP                                                   .0               .00
  12.  WASTE DISPOSAL                                                .0               .00
  13.  OTHER                                                         .0               .00
  14.        TOTAL INDIRECT COST                                  238.5             11.10
  15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                     631.5             29.37
  16.  TAXES, 2% OF FIXED CAPITAL                                 126.3              5.87
  17.  INSURANCE, 1% OF FIXED CAPITAL                              63.2              2.94
  18.  OTHER                                                         .0               .00
  19.        TOTAL FIXED COST                                     821.0             38.19

  20.  TOTAL OPERATING COST                                      2150.0            100.00
  21.  COST:  $/TON OF COAL                  .669
              MIL/KWH                        .194
```

IRON OXIDE REGENERATOR

```
                                   INPUT FOR FLUIDIZED BED

FLOW RATE (SCFM)                       111800.000       DENSITY OF SOLID (LBS/FT**3)            100.000
PARTICLE DIAMETER (INCHES)                 .0300        INLET CONCENT. (MOLE PERCENT)          10.00000
REACTION RATE (1/SEC)                   10.00000        OUTLET CONCENT. (MOLE PERCENT)          1.00000
RATIO- SUPERFICIAL TO MIN. VEL.            9.000        VOL. WAKE / VOL. BUBBLE                    .320
TEMPERATURE (DEG. F.)                   1112.000        FRACTION OF SOLIDS IN BUBBLE               .000
INLET PRESSURE (PSIA)                     14.700


                                   OUTPUT FROM FLUIDIZED BED

FLOW RATE (ACFM)                      337178.740        INITIAL BUBBLE DIAMETER (FEET)             .222
DIAMETER OF BED (FEET)                    38.431        FINAL BUBBLE DIAMETER (FEET)               .328
HEIGHT OF BED (FEET)                       2.537        INITIAL BUBBLE VEL. (FT/SEC)              6.205
HEIGHT OF VESSEL (FEET)                   19.216        FINIAL BUBBLE VEL. (FT/SEC)               6.617
THICKNESS OF SHELL (INCHES)                 .250        MIN. MASS FLUX (LBS/HR-FT**2)            50.423
BED PRESSURE DROP (IN. WATER)              4.991        MIN. FLUID VOIDAGE                         .463
DISTR. PRESS. DROP (IN. WATER)             1.685        MIN. FLUID VEL. (FT/SEC)                   .538
TOTAL PRESS. DROP (IN. WATER)              6.677        HOLES/IN.**2 IN DISTR. PLATE               .666
OUTLET PRESSURE (PSIA)                    14.459        PARTICLE TERMINAL VEL. (FT/SEC)          13.468
WEIGHT OF SORBENT (LBS)                 30178.741       SUPERFICIAL VELOCITY (FT/SEC)             4.846
FRACTION OF SOLIDS IN CLOUD                1.804        FRACTIONS OF BUBBLES IN BED                .813
FRACTION OF SOLIDS IN EMULSION            -1.584
```

IRON OXIDE REGENERATOR

```
PAGE  3                                                                          26 JUN 1969
                                   INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)              39.431          SHELL HEIGHT (FEET)                   19.216
  SHELL THICKNESS (INCHES)                    .250          CURRENT COST INDEX                   279.100


                                 OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (LBS)                  55241.761          LINING COST (DOLLARS)                  1695.
  WEIGHT OF HEADS (LBS)                  55241.761          COST OF VESSEL (DOLLARS)              39175.
  WEIGHT OF DISTR. PLATE (LBS)           34422.521          TOTAL COST OF SORBER (DOLLARS)        40871.
  WEIGHT OF VESSEL (LBS)                144906.040
```

IRON OXIDE REGENERATOR

```
PAGE  5                                                                                     25 JUN 1969
                                         INPUT PARAMETERS FOR CYCLONE

  CYCLONE REMOVAL EFFICIENCY (%)            98.000          PRESSURE DROP (INCHES WATER)              5.000
  FLUID DENSITY (LBS/FT**3)                   .026          SOLID DENSITY (LBS/FT**3)               100.000
  VISCOSITY (LBS/FT-SEC)                .00001574          WALL THICKNESS (INCHES)                    .250
  EFFECTIVE TURNS                           3.500          CURRENT COST INDEX                       279.100
  INPUT FLOW RATE (ACFM)               337178.740          NUMBER OF CYCLONES                            4.


                                        OUTPUT PARAMETERS FOR CYCLONE


                                        INDIVIDUAL CYCLONE PARAMETERS


  INPUT FLOW RATE (ACFM)                84294.683          INLET VELOCITY (FT/SEC)                   89.531
  CYCLONE DIAMETER (FEET)                  11.205          CYCLONE WEIGHT (LBS)                   19636.740
  PART. SIZE (MICRONS)- 98.0% EFF.         29.594          COST OF EACH CYCLONE (DOLLARS)             7542.
  PART. SIZE (MICRONS)- 50% EFF.           17.504

  TOTAL COST OF ALL CYCLONE UNITS          30169.
```

IRON OXIDE REGENERATOR

```
                              INPUT VARIABLES FOR FAN COST

COST INDEX AS OF MAY 5,1969        279.100        TOTAL FAN CAPACITY (ACFM)         337178.740
FAN SPEED (RPM)                   1200.000        AIR DENSITY (LBS/FT**3)                 .026
OVERALL EFFICIENCY                    .850        FAN PRESSURE DROP (IN. WATER)         11.577
NUMBER OF FAN UNITS                     1.


                          FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                              INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)             337178.740        WHEEL DIAMETER (INCHES)               79.076
DRIVER BRAKE HORSEPOWER            727.210        FAN COST (DOLLARS)                    30106.
ACTUAL DRIVER HORSEPOWER          1055.627        MOTOR COST (DOLLARS)                  11948.
FRACTIONAL CAPACITY PER FAN          1.000        EACH FAN UNIT COST (DOLLARS)          42053.

KILOWATTS REQUIRED BY DRIVER(S)    542.289        COST - ALL FAN UNITS (DOLLARS)        42053.
```

IRON OXIDE REGENERATOR

```
                                SO2 REMOVAL FROM FLUE GAS
                                        CATEGORY
                                   DRY METAL OXIDES
                              CAPITAL COST ESTIMATE SUMMARY
                                     CASE NO. 109.

               NAME OF PROCESS                          NAME OF EQUIPMENT
                   TRACOR                                REGENERATION UNIT

      FLUE GAS RATE      .1 MMSCFM                                     MW 1400.0

--------------------------------------------------------------------------------------------

                  ITEM                                  COST- THOU. $          % OF TOTAL
                  ----                                  -------------          ----------

       1.  PURCHASED EQUIPMENT                               113.1                19.22
       2.  ERECTION LABOR                                     28.3                 4.80
       3.  FOUNDATION & PLATFORMS                             20.4                 3.46
       4.  PIPING                                             84.8                14.41
       5.  INSTRUMENTS                                        17.0                 2.89
       6.  INSULATION                                          9.0                 1.54
       7.  ELECTRICAL                                         11.3                 1.92
       8.  BUILDINGS                                          28.3                 4.80
       9.  LAND & YARD IMPROVEMENTS                           14.7                 2.50
      10.  UTILITIES                                          45.2                 7.69
      11.        PHYSICAL-PLANT COST                         372.1                63.23
      12.  ENGINEERING & CONSTRUCTION                         74.6                12.68

      13.        DIRECT PLANT COST                           446.7                75.92
      14.  CONTRACTOR-S FEE                                   21.5                 3.65
      15.  CONTINGENCY                                        66.7                11.34

      16.        FIXED CAPITAL COST                          534.9                90.31
      17.  WORKING CAPITAL                                    53.5                 9.09

                 TOTAL INVESTMENT                            588.4               100.00
      18.  CAPITAL REQUIREMENTS
                $/KW CAPACITY                  .4
```

```
                          IRON OXIDE REGENERATOR                           26 JUN 1969
                         SO2 REMOVAL FROM FLUE GAS
                                 CATEGORY
                             DRY METAL OXIDES

                       OPERATING COST ESTIMATE SUMMARY
                    BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

              NAME OF PROCESS                       NAME OF EQUIPMENT
                   TRACOR                            REGENERATION UNIT

     FLUE GAS RATE      .1 MMSCFM                                 MW 1400.0
                              FIXED CAPITAL COST    534931.8

----------------------------------------------------------------------------------

                   ITEM                                COST- THOU. $      % OF TOTAL
                   ----                                -------------      ----------

     1.  RAW MATERIALS & CHEMICALS                              .0             .00
     2.  DIRECT LABOR                                           .0             .00
     3.  SUPERVISION                                            .0             .00
     4.  MAINTENANCE, 5% OF FIXED CAPITAL                     26.7            7.05
     5.  SUPPLIES, 15% OF MAINTENANCE                          4.0            1.06
     6.  UTILITIES                                            18.1            4.76
     7.  OTHER                                               245.6           64.74
     8.        TOTAL DIRECT COST                             294.4           77.61
     9.  PAYROLL BURDEN, 20% OF 2 & 3                           .0             .00
    10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                   15.4            4.05
    11.  PACK & SHIP                                            .0             .00
    12.  WASTE DISPOSAL                                         .0             .00
    13.  OTHER                                                  .0             .00
    14.        TOTAL INDIRECT COST                            15.4            4.05
    15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR               53.5           14.10
    16.  TAXES, 2% OF FIXED CAPITAL                           10.7            2.82
    17.  INSURANCE, 1% OF FIXED CAPITAL                        5.3            1.41
    18.  OTHER                                                  .0             .00
    19.        TOTAL FIXED COST                               69.5           18.33

    20.  TOTAL OPERATING COST                                379.5          100.00
    21.  COST:  $/TON OF COAL                 .113
               MIL/KWH                        .034
```

IRON OXIDE SORBER

```
PAGE  1                                                                      26 JUN 1969
                                 INPUT FOR FLUIDIZED BED

FLOW RATE (SCFM)                      500000.000       DENSITY OF SOLID (LBS/FT**3)         100.000
PARTICLE DIAMETER (INCHES)               .0300         INLET CONCENT. (MOLE PERCENT)         .00300
REACTION RATE (1/SEC)                  68.00000        OUTLET CONCENT. (MOLE PERCENT)        .00030
RATIO- SUPERFICIAL TO MIN. VEL.          5.000         VOL. WAKE / VOL. BUBBLE                 .320
TEMPERATURE (DEG. F.)                  649.000         FRACTION OF SOLIDS IN BUBBLE            .000
INLET PRESSURE (PSIA)                   14.700


                                 OUTPUT FROM FLUIDIZED BED

FLOW RATE (ACFM)                     1064575.200       INITIAL BUBBLE DIAMETER (FEET)          .207
DIAMETER OF BED (FEET)                  62.559         FINAL BUBBLE DIAMETER (FEET)            .328
HEIGHT OF BED (FEET)                     1.665         INITIAL BUBBLE VEL. (FT/SEC)           6.961
HEIGHT OF VESSEL (FEET)                 31.225         FINIAL BUBBLE VEL. (FT/SEC)            7.437
THICKNESS OF SHELL (INCHES)               .312         MIN. MASS FLUX (LBS/HR-FT**2)         35.167
BED PRESSURE DROP (IN. WATER)            2.306         MIN. FLUID VOIDAGE                      .458
DISTR. PRESS. DROP (IN. WATER)            .782         MIN. FLUID VEL. (FT/SEC)                .641
TOTAL PRESS. DROP (IN. WATER)            3.088         HOLES/IN.**2 IN DISTR. PLATE           1.386
OUTLET PRESSURE (PSIA)                  14.583         PARTICLE TERMINAL VEL. (FT/SEC)       11.963
WEIGHT OF SORBENT (LBS)              36983.595         SUPERFICIAL VELOCITY (FT/SEC)          5.769
FRACTION OF SOLIDS IN CLOUD              2.672         FRACTIONS OF BUBBLES IN BED             .867
FRACTION OF SOLIDS IN EMULSION          -2.496
```

```
PAGE  3                               IRON OXIDE SORBER                                      26 JUN 1969
                                  INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)            62.539        SHELL HEIGHT (FEET)                     31.295
  SHELL THICKNESS (INCHES)                  .312        CURRENT COST INDEX                     279.100


                                 OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (LBS)               132976.400        LINING COST (DOLLARS)                    4496.
  WEIGHT OF HEADS (LBS)               182976.400        COST OF VESSEL (DOLLARS)               109996.
  WEIGHT OF DISTR. PLATE (LBS)         91300.000        TOTAL COST OF SORBER (DOLLARS)         114492.
  WEIGHT OF VESSEL (LBS)              457252.810
```

IRON OXIDE SORBER

```
                                                                                          25 JUN 1969
                                        INPUT PARAMETERS FOR CYCLONE

CYCLONE REMOVAL EFFICIENCY (%)           98.000          PRESSURE DROP (INCHES WATER)             5.000
FLUID DENSITY (LBS/FT**3)                  .037          SOLID DENSITY (LBS/FT**3)              100.000
VISCOSITY (LBS/FT-SEC)                .00002061          WALL THICKNESS (INCHES)                   .250
EFFECTIVE TURNS                           3.500          CURRENT COST INDEX                     279.100
INPUT FLOW RATE (ACFM)              1064675.200          NUMBER OF CYCLONES                          4.


                                        OUTPUT PARAMETERS FOR CYCLONE


                                        INDIVIDUAL CYCLONE PARAMETERS


INPUT FLOW RATE (ACFM)               266168.770          INLET VELOCITY (FT/SEC)                 75.166
CYCLONE DIAMETER (FEET)                  21.731          CYCLONE WEIGHT (LBS)                 73855.474
PART. SIZE (MICRONS)- 98.% EFF.          40.253          COST OF EACH CYCLONE (DOLLARS)          28369.
PART. SIZE (MICRONS)- 50% EFF.           23.809

TOTAL COST OF ALL CYCLONE UNITS         113470.
```

IRON OXIDE SORBER

```
                                   INPUT VARIABLES FOR FAN COST

 COST INDEX AS OF MAY 5,1963              279.100       TOTAL FAN CAPACITY (ACFM)          1064675.200
 FAN SPEED (RPM)                         1200.000       AIR DENSITY (LBS/FT**3)                   .037
 OVERALL EFFICIENCY                          .850       FAN PRESSURE DROP (IN. WATER)            8.038
 NUMBER OF FAN UNITS                           1.


                              FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                                  INDIVIDUAL FAN UNIT PARAMETERS

 FAN CAPACITY (ACFM)                  1064675.100       WHEEL DIAMETER (INCHES)                 70.891
 DRIVER BRAKE HORSEPOWER                 1590.523       FAN COST (DOLLARS)                      22760.
 ACTUAL DRIVER HORSEPOWER                2308.824       MOTOR COST (DOLLARS)                    25129.
 FRACTIONAL CAPACITY PER FAN                1.000       EACH FAN UNIT COST (DOLLARS)            47888.

 KILOWATTS REQUIRED BY DRIVER(S)         1186.073       COST - ALL FAN UNITS (DOLLARS)          47888.
```

IRON OXIDE SORBER

```
PAGE   9                                                                   26 JUN 1969
                               SO2 REMOVAL FROM FLUE GAS
                                        CATEGORY
                                   DRY METAL OXIDES
                             CAPITAL COST ESTIMATE SUMMARY
                                     CASE NO. 105.

                   NAME OF PROCESS                     NAME OF EQUIPMENT
                       TRACOR                           SORPTION UNIT

           FLUE GAS RATE     .5 MMSCFM                                    MW  220.0

-----------------------------------------------------------------------------------

                      ITEM                             COST- THOU. $       % OF TOTAL
                      ----                             -------------       ----------

        1.  PURCHASED EQUIPMENT                                275.9            19.22
        2.  ERECTION LABOR                                      69.0             4.80
        3.  FOUNDATION & PLATFORMS                              49.7             3.46
        4.  PIPING                                             206.9            14.41
        5.  INSTRUMENTS                                         41.4             2.88
        6.  INSULATION                                          22.1             1.54
        7.  ELECTRICAL                                          27.6             1.92
        8.  BUILDINGS                                           69.0             4.80
        9.  LAND & YARD IMPROVEMENTS                            35.9             2.50
       10.  UTILITIES                                          110.3             7.69
       11.        PHYSICAL-PLANT COST                          907.5            63.23
       12.  ENGINEERING & CONSTRUCTION                         182.1            12.68

       13.        DIRECT PLANT COST                           1089.6            75.92
       14.  CONTRACTOR-S FEE                                    52.4             3.55
       15.  CONTINGENCY                                        162.8            11.34

       16.        FIXED CAPITAL COST                          1304.8            90.91
       17.  WORKING CAPITAL                                    130.5             9.09

                  TOTAL INVESTMENT                            1435.2           100.00
       18.  CAPITAL REQUIREMENTS
                  $/KW CAPACITY               6.5
```

IRON OXIDE SORBER

```
                                                                       26 JUN 1969
                          SO2 REMOVAL FROM FLUE GAS
                                  CATEGORY
                              DRY METAL OXIDES

                       OPERATING COST ESTIMATE SUMMARY
                    BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

              NAME OF PROCESS                      NAME OF EQUIPMENT
                  TRACOR                            SORPTION UNIT

      FLUE GAS RATE     .5 MMSCFM                                   MW  220.0
                            FIXED CAPITAL COST   1304772.4

-----------------------------------------------------------------------------------

                  ITEM                                COST- THOU. $     % OF TOTAL
                  ----                                -------------     ----------

  1.  RAW MATERIALS & CHEMICALS                               125.1          23.12
  2.  DIRECT LABOR                                             54.0           9.98
  3.  SUPERVISION                                              27.4           5.06
  4.  MAINTENANCE, 5% OF FIXED CAPITAL                         65.2          12.06
  5.  SUPPLIES, 15% OF MAINTENANCE                              9.8           1.81
  6.  UTILITIES                                                39.5           7.30
  7.  OTHER                                                   -44.2          -8.17
  8.        TOTAL DIRECT COST                                 276.8          51.17
  9.  PAYROLL BURDEN, 20% OF 2 & 3                             16.3           3.01
 10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                       78.2          14.46
 11.  PACK & SHIP                                                .0            .00
 12.  WASTE DISPOSAL                                             .0            .00
 13.  OTHER                                                      .0            .00
 14.        TOTAL INDIRECT COST                                94.5          17.47
 15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                  130.5          24.12
 16.  TAXES, 2% OF FIXED CAPITAL                               26.1           4.82
 17.  INSURANCE, 1% OF FIXED CAPITAL                           13.0           2.41
 18.  OTHER                                                      .0            .00
 19.        TOTAL FIXED COST                                  169.6          31.36

 20.  TOTAL OPERATING COST                                    540.9         100.00
 21.  COST:  $/TON OF COAL               1.084
              MIL/KWH                    .310
```

```
PAGE  1                              IRON OXIDE REGENERATOR                                      26 JUN 1969

                                   INPUT FOR FLUIDIZED BED

FLOW RATE (SCFM)                       21152.000        DENSITY OF SOLID (LBS/FT**3)          100.000
PARTICLE DIAMETER (INCHES)                 .0300        INLET CONCENT. (MOLE PERCENT)        10.00000
REACTION RATE (1/SEC)                   10.00000        OUTLET CONCENT. (MOLE PERCENT)        1.00000
RATIO- SUPERFICIAL TO MIN. VEL.            9.000        VOL. WAKE / VOL. BUBBLE                  .320
TEMPERATURE (DEG. F.)                   1112.000        FRACTION OF SOLIDS IN BUBBLE             .000
INLET PRESSURE (PSIA)                     14.700


                                   OUTPUT FROM FLUIDIZED BED

FLOW RATE (ACFM)                       53306.851        INITIAL BUBBLE DIAMETER (FEET)           .222
DIAMETER OF BED (FEET)                    15.731        FINAL BUBBLE DIAMETER (FEET)             .328
HEIGHT OF BED (FEET)                       7.597        INITIAL BUBBLE VEL. (FT/SEC)            6.205
HEIGHT OF VESSEL (FEET)                    8.366        FINIAL BUBBLE VEL. (FT/SEC)             6.617
THICKNESS OF SHELL (INCHES)                 .250        MIN. MASS FLUX (LBS/HR-FT**2)          50.423
BED PRESSURE DROP (IN. WATER)              4.991        MIN. FLUID VOIDAGE                       .463
DISTR. PRESS. DROP (IN. WATER)             1.685        MIN. FLUID VEL. (FT/SEC)                 .538
TOTAL PRESS. DROP (IN. WATER)              6.677        HOLES/IN.**2 IN DISTR. PLATE             .666
OUTLET PRESSURE (PSIA)                    14.459        PARTICLE TERMINAL VEL. (FT/SEC)        13.468
WEIGHT OF SORBENT (LBS)                 5719.393        SUPERFICIAL VELOCITY (FT/SEC)           4.846
FRACTION OF SOLIDS IN CLOUD                1.804        FRACTIONS OF BUBBLES IN BED              .813
FRACTION OF SOLIDS IN EMULSION            -1.584
```

IRON OXIDE REGENERATOR

```
PAGE   7                                                                              26 JUN 1969
                                     INPUT PARAMETERS FOR SORBER

  INSIDE SHELL DIAMETER (FEET)              15.731          SHELL HEIGHT (FEET)                    8.366
  SHELL THICKNESS (INCHES)                    .250          CURRENT COST INDEX                   279.100


                                   OUTPUT PARAMETERS FOR SORBER SHELL

  WEIGHT OF SHELL (LBS)                  10470.195          LINING COST (DOLLARS)                   321.
  WEIGHT OF HEADS (LBS)                  10470.195          COST OF VESSEL (DOLLARS)               8609.
  WEIGHT OF DISTR. PLATE (LBS)            6524.240          TOTAL COST OF SORBER (DOLLARS)         8930.
  WEIGHT OF VESSEL (LBS)                 27464.630
```

IRON OXIDE REGENERATOR

```
PAGE  5                                                                                        25 JUN 1969
                                       INPUT PARAMETERS FOR CYCLONE


  CYCLONE REMOVAL EFFICIENCY (%)          98.000        PRESSURE DROP (INCHES WATER)             5.000
  FLUID DENSITY (LBS/FT**3)                 .026        SOLID DENSITY (LBS/FT**3)              100.000
  VISCOSITY (LBS/FT-SEC)               .00002574        WALL THICKNESS (INCHES)                   .250
  EFFECTIVE TURNS                          3.500        CURRENT COST INDEX                     279.100
  INPUT FLOW RATE (ACFM)               63906.851        NUMBER OF CYCLONES                          4.


                                       OUTPUT PARAMETERS FOR CYCLONE


                                       INDIVIDUAL CYCLONE PARAMETERS


  INPUT FLOW RATE (ACFM)               15976.713        INLET VELOCITY (FT/SEC)                 89.531
  CYCLONE DIAMETER (FEET)                  4.878        CYCLONE WEIGHT (LBS)                  3721.831
  PART. SIZE (MICRONS)- 98.0% EFF.        19.527        COST OF EACH CYCLONE (DOLLARS)           1430.
  PART. SIZE (MICRONS)- 50% EFF.          11.550

  TOTAL COST OF ALL CYCLONE UNITS          5718.
```

```
                              INPUT VARIABLES FOR FAN COST

COST INDEX AS OF MAY 5,1969        273.100          TOTAL FAN CAPACITY (ACFM)          63906.851
FAN SPEED (RPM)                   1200.000          AIR DENSITY (LBS/FT**3)                 .026
OVERALL EFFICIENCY                    .330          FAN PRESSURE DROP (IN. WATER)         11.677
NUMBER OF FAN UNITS                     1.


                         FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                             INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)              63906.851          WHEEL DIAMETER (INCHES)                65.637
DRIVER BRAKE HORSEPOWER            137.831          FAN COST (DOLLARS)                     18687.
ACTUAL DRIVER HORSEPOWER           200.077          MOTOR COST (DOLLARS)                    2461.
FRACTIONAL CAPACITY PER FAN          1.000          EACH FAN UNIT COST (DOLLARS)           21148.

KILOWATTS REQUIRED BY DRIVER(S)    102.782          COST - ALL FAN UNITS (DOLLARS)         21148.
```

IRON OXIDE REGENERATOR

```
PAGE  9                                                                                 25 JUN 1969

                                    SO2 REMOVAL FROM FLUE GAS
                                             CATEGORY
                                        DRY METAL OXIDES
                                   CAPITAL COST ESTIMATE SUMMARY
                                          CASE NO. 199.

                   NAME OF PROCESS                       NAME OF EQUIPMENT
                       TRACOR                             REGENERATION UNIT

           FLUE GAS RATE      .0 MMSCFM                                         MW  220.0

--------------------------------------------------------------------------------------------------

                         ITEM                                   COST- THOU. $        % OF TOTAL
                         ----                                   -------------        ----------

           1.   PURCHASED EQUIPMENT                                     35.8              19.22
           2.   ERECTION LABOR                                           8.9               4.80
           3.   FOUNDATION & PLATFORMS                                   6.4               3.46
           4.   PIPING                                                  26.8              14.41
           5.   INSTRUMENTS                                              5.4               2.88
           6.   INSULATION                                               2.9               1.54
           7.   ELECTRICAL                                               3.6               1.92
           8.   BUILDINGS                                                8.9               4.80
           9.   LAND & YARD IMPROVEMENTS                                 4.7               2.50
          10.   UTILITIES                                               14.3               7.69
          11.         PHYSICAL-PLANT COST                              117.8              63.23
          12.   ENGINEERING & CONSTRUCTION                              23.6              12.68

          13.         DIRECT PLANT COST                                141.4              75.92
          14.   CONTRACTOR-S FEE                                         6.8               3.65
          15.   CONTINGENCY                                             21.1              11.34

          16.         FIXED CAPITAL COST                               169.3              90.91
          17.   WORKING CAPITAL                                         16.9               9.09

                      TOTAL INVESTMENT                                 186.3             100.00
          18.   CAPITAL REQUIREMENTS
                      $/KW CAPACITY                         .8
```

IRON OXIDE REGENERATOR

```
PAGE 10                                                                                    26 JUN 1969

                                      SO2 REMOVAL FROM FLUE GAS
                                              CATEGORY
                                          DRY METAL OXIDES

                                    OPERATING COST ESTIMATE SUMMARY
                                 BASIS:  330 DAY/YEAR 3   70.0 % CAPACITY

                        NAME OF PROCESS                          NAME OF EQUIPMENT
                            TRACOR                                REGENERATION UNIT

          FLUE GAS RATE      .0 MMSCFM                                      MW  220.0
                                  FIXED CAPITAL COST     169318.3

----------------------------------------------------------------------------------------------

                        ITEM                                  COST- THOU. $          % OF TOTAL
                        ----                                  -------------          ----------

      1.  RAW MATERIALS & CHEMICALS                                     .0                 .00
      2.  DIRECT LABOR                                                  .0                 .00
      3.  SUPERVISION                                                   .0                 .00
      4.  MAINTENANCE, 5% OF FIXED CAPITAL                             8.5                9.80
      5.  SUPPLIES, 15% OF MAINTENANCE                                 1.3                1.47
      6.  UTILITIES                                                    3.4                3.96
      7.  OTHER                                                       46.3               53.65
      8.       TOTAL DIRECT COST                                      59.5               68.88
      9.  PAYROLL BURDEN, 20% OF 2 & 3                                  .0                 .00
     10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                           4.9                5.64
     11.  PACK & SHIP                                                   .0                 .00
     12.  WASTE DISPOSAL                                                .0                 .00
     13.  OTHER                                                         .0                 .00
     14.       TOTAL INDI        ST                                    4.9                5.64
     15.  DEPRECIATION, 1         IXED CAPITAL/YR                     16.9               19.60
     16.  TAXES, 2% OF FIXE        TAL                                 3.4                3.92
     17.  INSURANCE, 1% OF          APITAL                             1.7                1.96
     18.  OTHER                                                         .0                 .00
     19.       TOTAL FIXED C                                          22.0               25.48

     20.  TOTAL OPERATING COST                                        86.4              100.00
     21.  COST:  $/TON OF COAL                    .173
                 MIL/KWH                          .050
```

```
PAGE  1                                  IRON OXIDE SORBER                                        26 JUN 1969
                                      INPUT FOR FLUIDIZED BED


   FLOW RATE (SCFM)                       20000.000      DENSITY OF SOLID (LBS/FT**3)             100.000
   PARTICLE DIAMETER (INCHES)               .0300        INLET CONCENT. (MOLE PERCENT)            .02900
   REACTION RATE (1/SEC)                  68.00000       OUTLET CONCENT. (MOLE PERCENT)           .00500
   RATIO- SUPERFICIAL TO MIN. VEL.           9.000       VOL. WAKE / VOL. BUBBLE                    .320
   TEMPERATURE (DEG. F.)                   648.000       FRACTION OF SOLIDS IN BUBBLE               .000
   INLET PRESSURE (PSIA)                    14.700


                                     OUTPUT FROM FLUIDIZED BED


   FLOW RATE (ACFM)                       42587.005      INITIAL BUBBLE DIAMETER (FEET)             .207
   DIAMETER OF BED (FEET)                    12.518      FINAL BUBBLE DIAMETER (FEET)               .328
   HEIGHT OF BED (FEET)                       1.271      INITIAL BUBBLE VEL. (FT/SEC)              6.961
   HEIGHT OF VESSEL (FEET)                    6.259      FINIAL BUBBLE VEL. (FT/SEC)               7.437
   THICKNESS OF SHELL (INCHES)                 .250      MIN. MASS FLUX (LBS/HR-FT**2)            85.167
   BED PRESSURE DROP (IN. WATER)              1.757      MIN. FLUID VOIDAGE                         .458
   DISTR. PRESS. DROP (IN. WATER)              .596      MIN. FLUID VEL. (FT/SEC)                   .641
   TOTAL PRESS. DROP (IN. WATER)              2.352      HOLES/IN.**2 IN DISTR. PLATE              1.588
   OUTLET PRESSURE (PSIA)                    14.615      PARTICLE TERMINAL VEL. (FT/SEC)          11.963
   WEIGHT OF SORBENT (LBS)                 1126.985      SUPERFICIAL VELOCITY (FT/SEC)             5.769
   FRACTION OF SOLIDS IN CLOUD                2.672      FRACTIONS OF BUBBLES IN BED                .867
   FRACTION OF SOLIDS IN EMULSION            -2.495
```

IRON OXIDE SORBER

```
                              INPUT PARAMETERS FOR SORBER

INSIDE SHELL DIAMETER (FEET)        12.518        SHELL HEIGHT (FEET)                      6.259
SHELL THICKNESS (INCHES)              .250        CURRENT COST INDEX                     279.100


                            OUTPUT PARAMETERS FOR SORBER SHELL


WEIGHT OF SHELL (LBS)             5860.783        LINING COST (DOLLARS)                    180.
WEIGHT OF HEADS (LBS)             5960.733        COST OF VESSEL (DOLLARS)                5050.
WEIGHT OF DISTR. PLATE (LBS)      3552.000        TOTAL COST OF SORBER (DOLLARS)          5230.
WEIGHT OF VESSEL (LBS)           15373.565
```

IRON OXIDE SORBER

```
PAGE  3                                                                                  26 JUN 1969
                                          INPUT PARAMETERS FOR CYCLONE


  CYCLONE REMOVAL EFFICIENCY (%)          98.000            PRESSURE DROP (INCHES WATER)            5.000
  FLUID DENSITY (LBS/FT**3)                 .037            SOLID DENSITY (LBS/FT**3)             100.000
  VISCOSITY (LBS/FT-SEC)               .00002061            WALL THICKNESS (INCHES)                  .250
  EFFECTIVE TURNS                          3.500            CURRENT COST INDEX                    279.100
  INPUT FLOW RATE (ACFM)               42587.005            NUMBER OF CYCLONES                         2.


                                          OUTPUT PARAMETERS FOR CYCLONE


                                         INDIVIDUAL CYCLONE PARAMETERS


  INPUT FLOW RATE (ACFM)               21293.502            INLET VELOCITY (FT/SEC)                75.166
  CYCLONE DIAMETER (FEET)                  6.145            CYCLONE WEIGHT (LBS)                 5908.438
  PART. SIZE (MICRONS)- 98.% EFF.         21.408            COST OF EACH CYCLONE (DOLLARS)          2269.
  PART. SIZE (MICRONS)- 50% EFF.          12.662

  TOTAL COST OF ALL CYCLONE UNITS          4533.
```

```
                             INPUT VARIABLES FOR FAN COST

COST INDEX AS OF MAY 5,1969        279.100      TOTAL FAN CAPACITY (ACFM)           42587.005
FAN SPEED (RPM)                   1200.000      AIR DENSITY (LBS/FT**3)                  .037
OVERALL EFFICIENCY                    .850      FAN PRESSURE DROP (IN. WATER)           7.352
NUMBER OF FAN UNITS                     1.


                          FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                             INDIVIDUAL FAN UNIT PARAMETERS

FAN CAPACITY (ACFM)              42587.004      WHEEL DIAMETER (INCHES)                47.893
DRIVER BRAKE HORSEPOWER             57.835      FAN COST (DOLLARS)                     8340.
ACTUAL DRIVER HORSEPOWER            83.953      MOTOR COST (DOLLARS)                   1078.
FRACTIONAL CAPACITY PER FAN          1.000      EACH FAN UNIT COST (DOLLARS)           9418.

KILOWATTS REQUIRED BY DRIVER(S)     43.128      COST - ALL FAN UNITS (DOLLARS)         9418.
```

IRON OXIDE SORBER

```
PAGE  2                                                                          25 JUN 1969

                                  SO2 REMOVAL FROM FLUE GAS
                                          CATEGORY
                                     DRY METAL OXIDES
                                CAPITAL COST ESTIMATE SUMMARY
                                        CASE NO. 107.

                    NAME OF PROCESS                          NAME OF EQUIPMENT
                        TRACOR                                SORPTION UNIT

           FLUE GAS RATE      .0 MMSCFM                                       MW   13.8

--------------------------------------------------------------------------------------------

                      ITEM                                 COST- THOU. $         % OF TOTAL
                      ----                                 -------------         ----------

          1.   PURCHASED EQUIPMENT                                  19.2              19.22
          2.   ERECTION LABOR                                        4.8               4.80
          3.   FOUNDATION & PLATFORMS                                3.5               3.46
          4.   PIPING                                               14.4              14.41
          5.   INSTRUMENTS                                           2.9               2.88
          6.   INSULATION                                            1.5               1.54
          7.   ELECTRICAL                                            1.9               1.92
          8.   BUILDINGS                                             4.8               4.80
          9.   LAND & YARD IMPROVEMENTS                              2.5               2.50
         10.   UTILITIES                                             7.7               7.69
         11.        PHYSICAL-PLANT COST                             63.1              63.23
         12.   ENGINEERING & CONSTRUCTION                           12.7              12.68

         13.        DIRECT PLANT COST                               75.8              75.92
         14.   CONTRACTOR-S FEE                                      3.6               3.65
         15.   CONTINGENCY                                          11.3              11.34

         16.        FIXED CAPITAL COST                              90.3              90.91
         17.   WORKING CAPITAL                                       9.1               9.09

                    TOTAL INVESTMENT                                99.8             100.00
         18.   CAPITAL REQUIREMENTS
                    $/KW CAPACITY                     7.2
```

IRON OXIDE SORBER

```
                      SO2 REMOVAL FROM FLUE GAS
                              CATEGORY
                          DRY METAL OXIDES

                    OPERATING COST ESTIMATE SUMMARY
                BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

            NAME OF PROCESS                    NAME OF EQUIPMENT
                 TRACOR                         SORPTION UNIT

   FLUE GAS RATE      .0 MMSCFM                               MW   13.8
                         FIXED CAPITAL COST     90754.6
----------------------------------------------------------------------------

            ITEM                                COST- THOU. $      % OF TOTAL
            ----                                -------------      ----------

  1.  RAW MATERIALS & CHEMICALS                          44.9           23.92
  2.  DIRECT LABOR                                       54.0           28.76
  3.  SUPERVISION                                        27.4           14.59
  4.  MAINTENANCE, 5% OF FIXED CAPITAL                    4.5            2.42
  5.  SUPPLIES, 15% OF MAINTENANCE                         .7             .36
  6.  UTILITIES                                           1.4             .76
  7.  OTHER                                             -16.6           -8.84
  8.        TOTAL DIRECT COST                           116.4           61.98
  9.  PAYROLL BURDEN, 20% OF 2 & 3                       16.3            8.67
 10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                 43.3           23.07
 11.  PACK & SHIP                                          .0             .00
 12.  WASTE DISPOSAL                                       .0             .00
 13.  OTHER                                                .0             .00
 14.        TOTAL INDIRECT COST                          59.6           31.74
 15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR              9.1            4.83
 16.  TAXES, 2% OF FIXED CAPITAL                          1.8             .97
 17.  INSURANCE, 1% OF FIXED CAPITAL                       .9             .48
 18.  OTHER                                                .0             .00
 19.        TOTAL FIXED COST                             11.8            6.28

 20.  TOTAL OPERATING COST                              187.7          100.00
 21.  COST:  $/TON OF COAL               6.064
             MIL/KWH                     1.714
```

```
                                IRON OXIDE REGENERATOR                                  25 JUN 1969
                                INPUT FOR FLUIDIZED BED

FLOW RATE (SCFM)                       7577.000
PARTICLE DIAMETER (INCHES)                .0300    DENSITY OF SOLID (LBS/FT**3)          100.000
REACTION RATE (1/SEC)                  10.00000    INLET CONCENT. (MOLE PERCENT)       10.00000
RATIO- SUPERFICIAL TO MIN. VEL.           9.000    OUTLET CONCENT. (MOLE PERCENT)       1.00000
TEMPERATURE (DEG. F.)                  1112.000    VOL. WAKE / VOL. BUBELE                 .320
INLET PRESSURE (PSIA)                    14.700    FRACTION OF SOLIDS IN BUBBLE            .000


                                OUTPUT FROM FLUIDIZED BED

FLOW RATE (ACFM)                      22892.503
DIAMETER OF BED (FEET)                   10.014    INITIAL BUBBLE DIAMETER (FEET)          .222
HEIGHT OF BED (FEET)                      2.597    FINAL BUBBLE DIAMETER (FEET)            .328
HEIGHT OF VESSEL (FEET)                   5.007    INITIAL BUBBLE VEL. (FT/SEC)           6.205
THICKNESS OF SHELL (INCHES)                .250    FINIAL BUBBLE VEL. (FT/SEC)            6.617
BED PRESSURE DROP (IN. WATER)             4.991    MIN. MASS FLUX (LBS/HR-FT**2)         50.423
DISTR. PRESS. DROP (IN. WATER)            1.685    MIN. FLUID VOIDAGE                      .463
TOTAL PRESS. DROP (IN. WATER)             6.677    MIN. FLUID VEL. (FT/SEC)                .538
OUTLET PRESSURE (PSIA)                   14.459    HOLES/IN.**2 IN DISTR. PLATE            .666
WEIGHT OF SORBENT (LBS)                2048.963    PARTICLE TERMINAL VEL. (FT/SEC)       13.468
FRACTION OF SOLIDS IN CLOUD               1.804    SUPERFICIAL VELOCITY (FT/SEC)          4.846
FRACTION OF SOLIDS IN EMULSION           -1.584    FRACTIONS OF BUBBLES IN BED             .813
```

IRON OXIDE REGENERATOR

```
                              INPUT PARAMETERS FOR SORBER

   INSIDE SHELL DIAMETER (FEET)            10.014        SHELL HEIGHT (FEET)                   5.007
   SHELL THICKNESS (INCHES)                  .250        CURRENT COST INDEX                  279.100


                            OUTPUT PARAMETERS FOR SORBER SHELL

   WEIGHT OF SHELL (LBS)                 3750.599        LINING COST (DOLLARS)                  115.
   WEIGHT OF HEADS (LBS)                 3750.599        COST OF VESSEL (DOLLARS)              3346.
   WEIGHT OF DISTR. PLATE (LBS)          2337.092        TOTAL COST OF SORBER (DOLLARS)        3461.
   WEIGHT OF VESSEL (LBS)                9838.289
```

IRON OXIDE REGENERATOR

```
                                   INPUT PARAMETERS FOR CYCLONE

CYCLONE REMOVAL EFFICIENCY (%)          98.000        PRESSURE DROP (INCHES WATER)            5.000
FLUID DENSITY (LBS/FT**3)                 .026        SOLID DENSITY (LBS/FT**3)             100.000
VISCOSITY (LBS/FT-SEC)               .00002574        WALL THICKNESS (INCHES)                  .250
EFFECTIVE TURNS                          7.500        CURRENT COST INDEX                    279.100
INPUT FLOW RATE (ACFM)               22892.503        NUMBER OF CYCLONES                         2.


                                   OUTPUT PARAMETERS FOR CYCLONE


                                   INDIVIDUAL CYCLONE PARAMETERS


INPUT FLOW RATE (ACFM)               11446.251        INLET VELOCITY (FT/SEC)                89.531
CYCLONE DIAMETER (FEET)                  4.129        CYCLONE WEIGHT (LBS)                 2666.444
PART. SIZE (MICRONS)- 99.% EFF.         17.965        COST OF EACH CYCLONE (DOLLARS)          1024.
PART. SIZE (MICRONS)- 50% EFF.          10.626

TOTAL COST OF ALL CYCLONE UNITS          2048.
```

```
PAGE  7                          IRON OXIDE REGENERATOR                              26 JUN 1969
                              INPUT VARIABLES FOR FAN COST

 COST INDEX AS OF MAY 5,1969         279.100         TOTAL FAN CAPACITY (ACFM)          22892.503
 FAN SPEED (RPM)                    1200.000         AIR DENSITY (LBS/FT**3)                 .026
 OVERALL EFFICIENCY                     .850         FAN PRESSURE DROP (IN. WATER)         11.677
 NUMBER OF FAN UNITS                      1.


                         FAN AND DRIVER MOTOR OUTPUT PARAMETERS


                            INDIVIDUAL FAN UNIT PARAMETERS


 FAN CAPACITY (ACFM)               22892.503         WHEEL DIAMETER (INCHES)               58.508
 DRIVER BRAKE HORSEPOWER              49.373         FAN COST (DOLLARS)                    13922.
 ACTUAL DRIVER HORSEPOWER             71.971         MOTOR COST (DOLLARS)                    928.
 FRACTIONAL CAPACITY PER FAN           1.000         EACH FAN UNIT COST (DOLLARS)          14850.

 KILOWATTS REQUIRED BY DRIVER(S)      36.818         COST - ALL FAN UNITS (DOLLARS)        14850.
```

IRON OXIDE REGENERATOR

```
                                   SO2 REMOVAL FROM FLUE GAS                          26 JUN 1963
                                           CATEGORY
                                      DRY METAL OXIDES
                                 CAPITAL COST ESTIMATE SUMMARY
                                         CASE NO. 199.

                       NAME OF PROCESS                        NAME OF EQUIPMENT
                           TRACOR                              REGENERATION UNIT

           FLUE GAS RATE      .0 MMSCFM
                                                                              MW   13.8
-----------------------------------------------------------------------------------------------

                         ITEM                                  COST- THOU. $         % OF TOTAL
                         ----                                  -------------         ----------

           1.  PURCHASED EQUIPMENT                                    20.4              19.22
           2.  ERECTION LABOR                                          5.1               4.80
           3.  FOUNDATION & PLATFORMS                                  3.7               3.46
           4.  PIPING                                                 15.3              14.41
           5.  INSTRUMENTS                                             3.1               2.88
           6.  INSULATION                                              1.6               1.54
           7.  ELECTRICAL                                              2.0               1.92
           8.  BUILDINGS                                               5.1               4.80
           9.  LAND & YARD IMPROVEMENTS                                2.6               2.50
          10.  UTILITIES                                               8.1               7.69
          11.        PHYSICAL-PLANT COST                              67.0              63.23
          12.  ENGINEERING & CONSTRUCTION                             13.4              12.68

          13.        DIRECT PLANT COST                                80.4              75.92
          14.  CONTRACTOR-S FEE                                        3.9               3.65
          15.  CONTINGENCY                                            12.0              11.34

          16.        FIXED CAPITAL COST                               96.3              90.91
          17.  WORKING CAPITAL                                         9.6               9.09

                     TOTAL INVESTMENT                                105.9             100.00
          18.  CAPITAL REQUIREMENTS
                     $/KW CAPACITY                   7.7
```

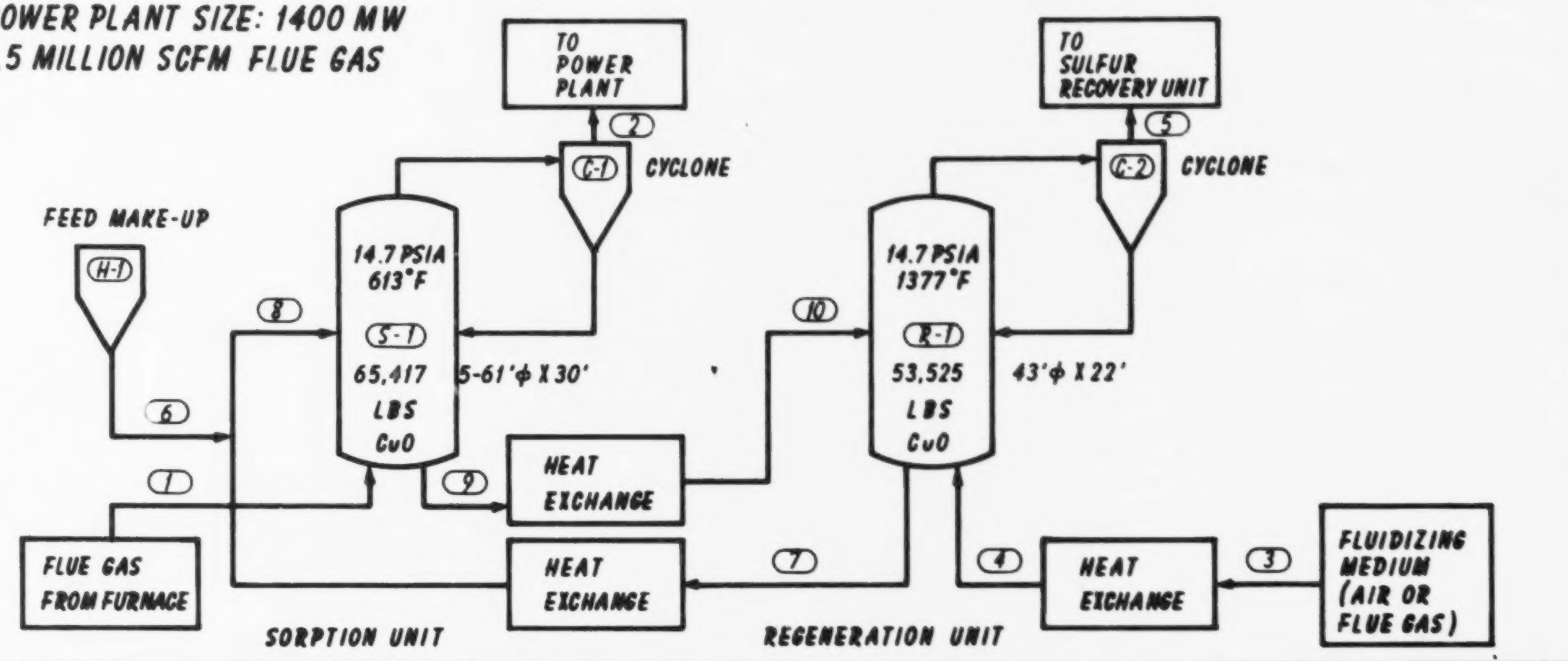
IRON OXIDE REGENERATOR

```
                               SO2 REMOVAL FROM FLUE GAS
                                       CATEGORY
                                   DRY METAL OXIDES

                           OPERATING COST ESTIMATE SUMMARY
                        BASIS:  330 DAY/YEAR @   70.0 % CAPACITY

              NAME OF PROCESS                           NAME OF EQUIPMENT
                  TRACOR                                 REGENERATION UNIT

     FLUE GAS RATE      .0 MMSCFM                                     MW    13.8
                              FIXED CAPITAL COST       96300.0

----------------------------------------------------------------------------------------

                 ITEM                                  COST- THOU. $         % OF TOTAL
                 ----                                  -------------         ----------

     1.  RAW MATERIALS & CHEMICALS                               .0                 .00
     2.  DIRECT LABOR                                            .0                 .00
     3.  SUPERVISION                                             .0                 .00
     4.  MAINTENANCE, 5% OF FIXED CAPITAL                       4.8               12.45
     5.  SUPPLIES, 15% OF MAINTENANCE                            .7                1.87
     6.  UTILITIES                                              1.2                3.17
     7.  OTHER                                                 16.6               43.00
     8.        TOTAL DIRECT COST                               23.4               60.43
     9.  PAYROLL BURDEN, 20% OF 2 & 3                            .0                 .00
    10.  PLANT OVERHEAD, 50% OF 2, 3, 4 & 5                     2.8                7.16
    11.  PACK & SHIP                                             .0                 .00
    12.  WASTE DISPOSAL                                          .0                 .00
    13.  OTHER                                                   .0                 .00
    14.        TOTAL INDIRECT COST                              2.8                7.16
    15.  DEPRECIATION,  10.0 % FIXED CAPITAL/YR                 9.6               24.90
    16.  TAXES, 2% OF FIXED CAPITAL                             1.9                4.98
    17.  INSURANCE, 1% OF FIXED CAPITAL                         1.0                2.49
    18.  OTHER                                                   .0                 .00
    19.        TOTAL FIXED COST                                12.5               32.36

    20.  TOTAL OPERATING COST                                  38.7              100.00
    21.  COST:  $/TON OF COAL                  1.243
                MIL/KWH                         .353
```

8.2 THERMODYNAMIC, KINETIC, AND ECONOMIC DATA

8.2.5 Process Flowsheets Including Heat and Material Balances

POWER PLANT SIZE: 1400 MW
2.5 MILLION SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA
613°F
S-1
65,417
LBS
CuO
5-61'ϕ X 30'
6
1
9
FLUE GAS FROM FURNACE
HEAT EXCHANGE
HEAT EXCHANGE
SORPTION UNIT
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
10
14.7 PSIA
1377°F
R-1
53,525
LBS
CuO
43'ϕ X 22'
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
REGENERATION UNIT

COMPONENT / STREAM	1	2	3	4	5	6	7	8	9	10
SO_2, MLB/HR	75.86	3.79	0.17	0.17	0.17					
SO_3, MLB/HR	-	-	-	-	90.09					
N_2, MLB/HR	8285.66	8285.66	371.61	371.61	371.61					
CO_2, MLB/HR	2555.39	2555.39	114.61	114.61	114.61					
H_2O, MLB/HR	515.58	515.58	23.12	23.12	23.12					
O_2, MLB/HR	353.99	335.98	15.07	15.07	15.07					
NO, MLB/HR	5.93	5.93	0.26	0.26	0.26					
TOTAL GAS, MLB/HR	11792.41	11702.33	524.84	524.84	614.93					
CuO, MLB/HR						0.12507	240.22	240.22	150.68	150.68
$CuSO_4$, MLB/HR							19.91	19.91	199.54	199.54
TOTAL SOLID, MLB/HR						0.12507	260.13	260.13	350.22	350.22
ENTHALPY, MM BTU/HR	1689.81	1680.44	-	194.43	224.41	-	54.28	20.76	30.14	80.43

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

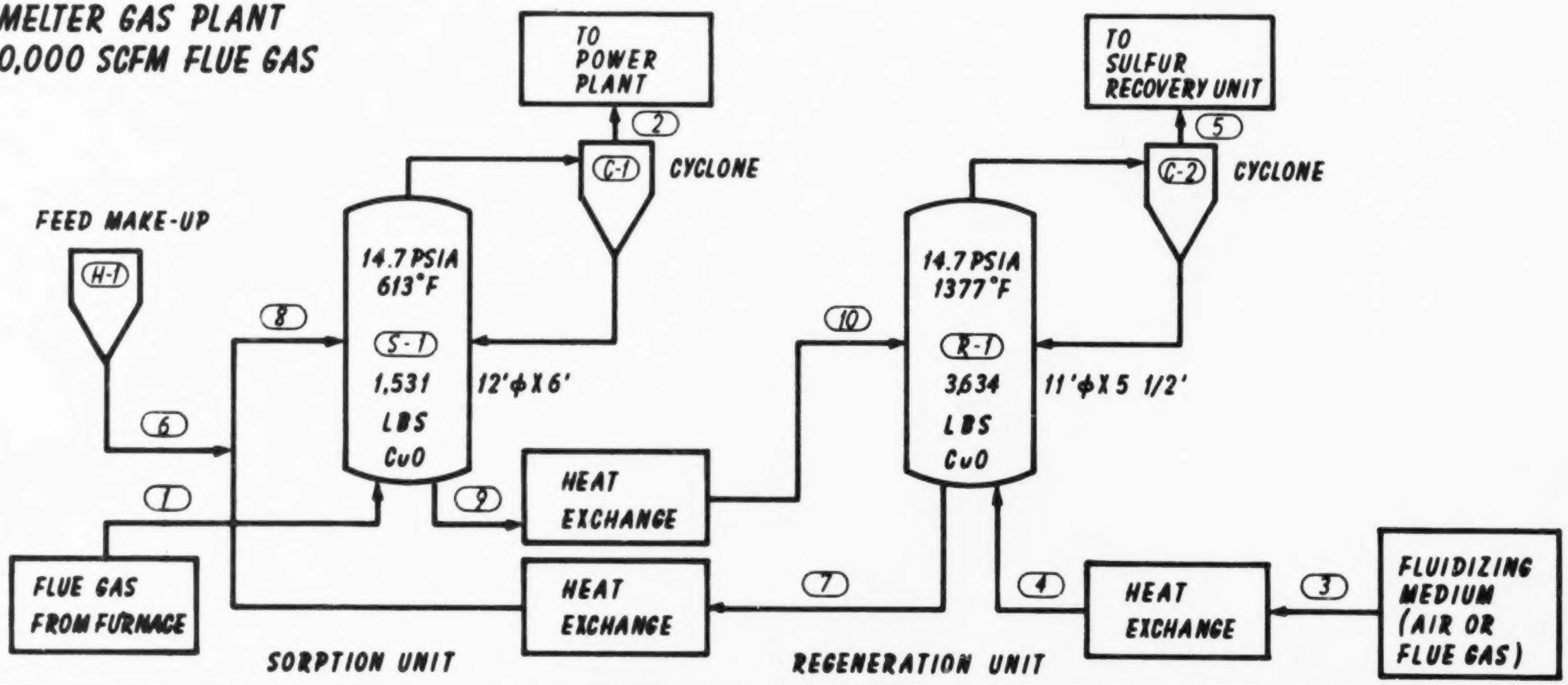
TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET

DATE - JUNE 30, 1969

A6-164-37

SMELTER GAS PLANT
20,000 SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
FEED MAKE-UP
H-1
6
8
14.7 PSIA
613°F
S-1
1,531
LBS
CuO
12'ΦX6'
7
1
9
FLUE GAS FROM FURNACE
HEAT EXCHANGE
HEAT EXCHANGE
10
14.7 PSIA
1377°F
R-1
3,634
LBS
CuO
11'ΦX5 1/2'
4
3
HEAT EXCHANGE
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
SORPTION UNIT
REGENERATION UNIT

COMPONENT / STREAM	1	2	3	4	5	6	7	8	9	10
SO_2, MLB/HR	5.87	0.97	0.38	0.38	0.38					
SO_3, MLB/HR	-	-	-	-	6.12					
N_2, MLB/HR	71.15	71.15	27.97	27.97	27.97					
CO_2, MLB/HR	2.36	2.36	0.93	0.93	0.93					
H_2O, MLB/HR	0.06	0.06	0.02	0.02	0.02					
O_2, MLB/HR	14.46	13.24	5.20	5.20	5.20					
CO, MLB/HR	0.53	0.53	0.21	0.21	0.21					
TOTAL GAS, MLB/HR	94.43	88.31	34.71	34.71	40.83					
CuO, MLB/HR						0.00849	16.30	16.30	10.19	10.19
$CuSO_4$, MLB/HR							1.36	1.36	13.63	13.63
TOTAL SOLID, MLB/HR						0.00849	17.66	17.66	23.82	23.82
ENTHALPY, MM BTU/HR	12.82	12.18	-	12.09	14.12	-	3.69	1.41	2.05	5.47

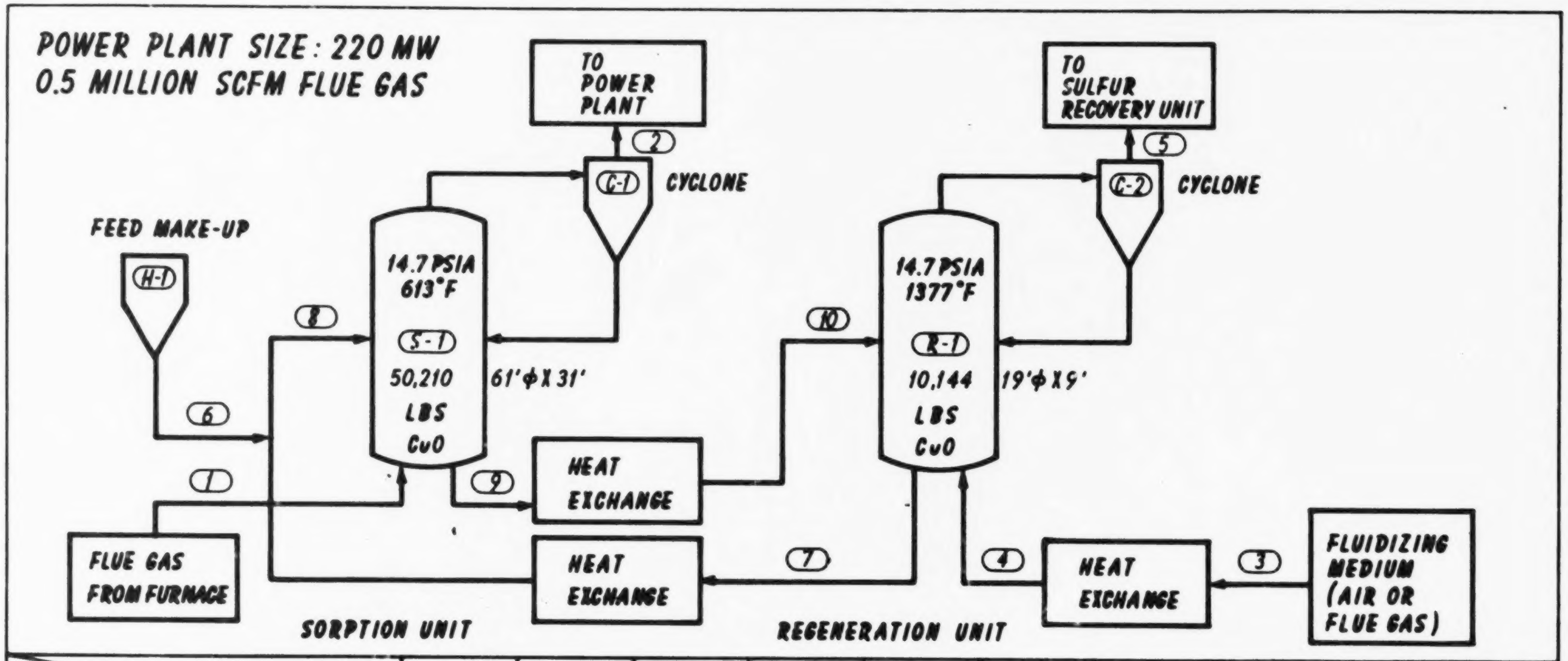
M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET DATE - JUNE 30, 1969

A6-164-37

A6-164-40


POWER PLANT SIZE: 220 MW
0.5 MILLION SCFM FLUE GAS
TO POWER PLANT
2
C-1
CYCLONE
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA
613°F
S-1
50,210
LBS
CuO
61'ϕX 31'
6
1
9
HEAT EXCHANGE
FLUE GAS FROM FURNACE
HEAT EXCHANGE
10
14.7 PSIA
1377°F
R-1
10,144
LBS
CuO
19'ϕX9'
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
SORPTION UNIT
REGENERATION UNIT

COMPONENT \ STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	15.17	1.52	0.06	0.06	0.06					
SO_3, MLB/HR	-	-	-	-	17.06					
N_2, MLB/HR	1657.13	1657.13	70.39	70.39	70.39					
CO_2, MLB/HR	511.08	511.08	21.71	21.71	21.71					
H_2O, MLB/HR	103.12	103.12	4.38	4.38	4.38					
O_2, MLB/HR	70.80	67.39	2.86	2.86	2.86					
NO, MLB/HR	1.18	1.18	0.05	0.05	0.05					
TOTAL GAS, MLB/HR	2358.48	2341.42	99.45	99.45	116.51					
CuO, MLB/HR						0.02370	45.51	45.51	37.80	37.80
$CuSO_4$, MLB/HR							3.78	3.78	28.55	28.55
TOTAL SOLID, MLB/HR						0.02370	49.29	49.29	66.35	66.35
ENTHALPY, MM BTU/HR	337.96	336.19	-	35.98	41.50	-	10.04	3.94	5.71	14.87

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

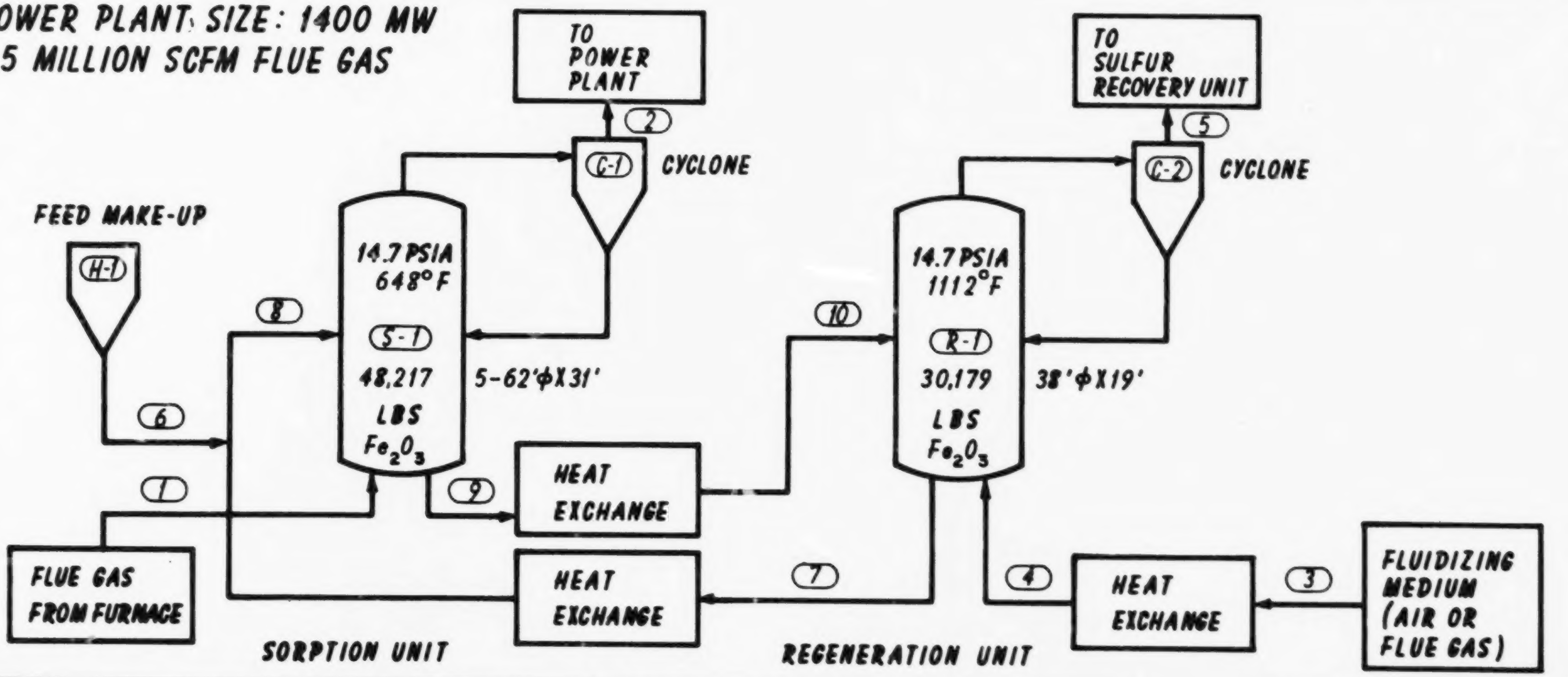
TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET

DATE - JUNE 30, 1969

A6-164-37

POWER PLANT SIZE: 1400 MW
2.5 MILLION SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA 648°F
S-1
48,217 LBS Fe_2O_3
5-62'ΦX31'
6
1
9
FLUE GAS FROM FURNACE
HEAT EXCHANGE
HEAT EXCHANGE
10
14.7 PSIA 1112°F
R-1
30,179 LBS Fe_2O_3
38'ΦX19'
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
SORPTION UNIT
REGENERATION UNIT

COMPONENT / STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	75.86	3.79	0.17	0.17	0.17					
SO_3, MLB/HR	-	-	-	-	90.09					
N_2, MLB/HR	8285.66	8285.66	371.61	371.61	371.61					
CO_2, MLB/HR	2555.39	2555.39	114.61	114.61	114.61					
H_2O, MLB/HR	515.58	515.58	23.12	23.12	23.12					
O_2, MLB/HR	353.99	335.98	15.07	15.07	15.07					
NO, MLB/HR	5.93	5.93	0.26	0.26	0.26					
TOTAL GAS, MLB/HR	1179241	1170233	524.84	524.84	614.93					
Fe_2O_3, MLB/HR						0.11913	231.60	231.60	171.61	171.61
$Fe_2(SO_4)_3$, MLB/HR							16.66	16.66	166.66	166.66
TOTAL SOLID, MLB/HR						0.11913	248.26	248.26	338.27	338.27
ENTHALPY, MM BTU/HR	1801.32	1791.28	-	151.18	173.36	-	56.31	29.17	40.61	79.54

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

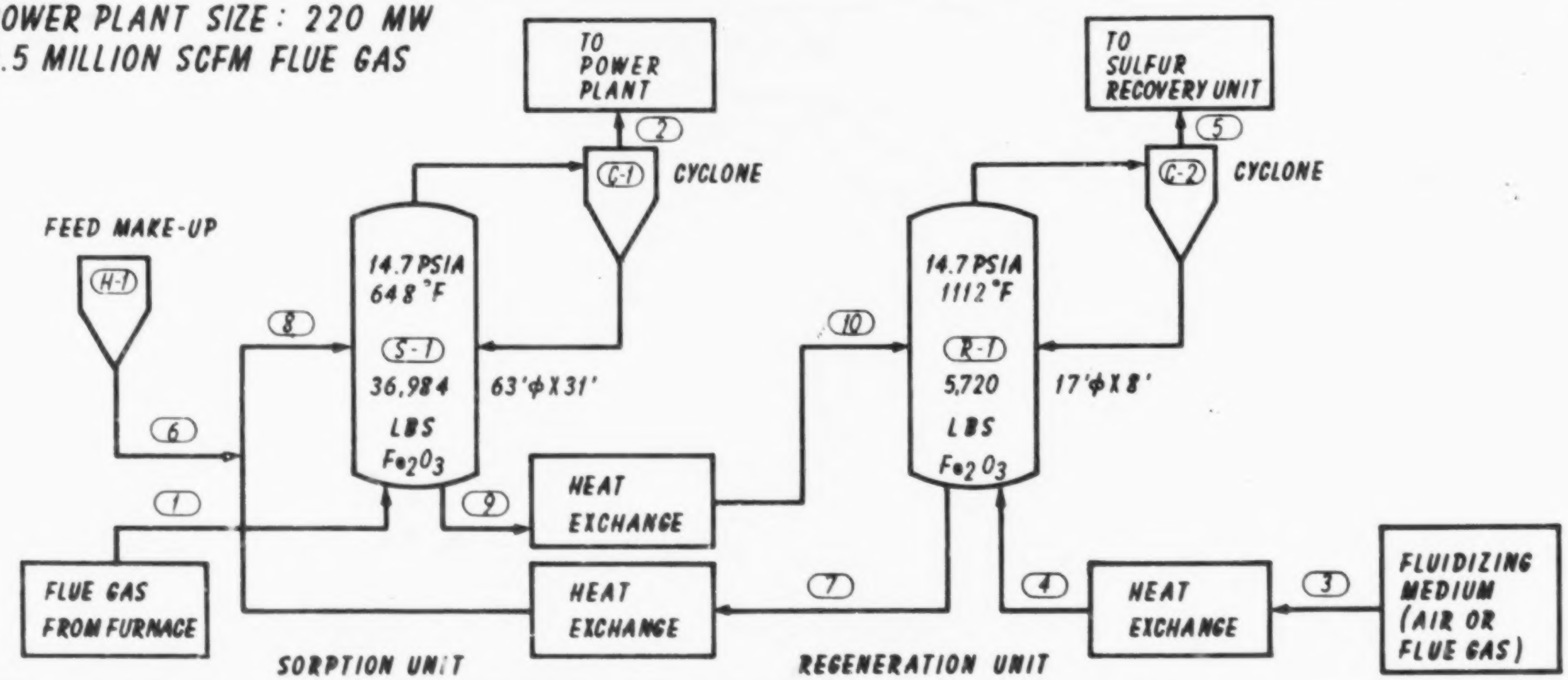
TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET DATE - JUNE 30, 1969

A6-164-37

A6-164-42

POWER PLANT SIZE : 220 MW
0.5 MILLION SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA
648 °F
S-1
36,984
LBS
Fe_2O_3
63'φ X 31'
10
14.7 PSIA
1112 °F
R-1
5,720
LBS
Fe_2O_3
17'φ X 8'
6
1
9
HEAT EXCHANGE
FLUE GAS FROM FURNACE
HEAT EXCHANGE
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
SORPTION UNIT
REGENERATION UNIT

COMPONENT \ STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	15.17	1.52	0.06	0.06	0.06					
SO_3, MLB/HR	-	-	-	-	17.06					
N_2, MLB/HR	1657.13	1657.13	70.39	70.39	70.39					
CO_2, MLB/HR	511.08	511.08	21.71	21.71	21.71					
H_2O, MLB/HR	103.12	103.12	4.38	4.38	4.38					
O_2, MLB/HR	70.80	67.39	2.86	2.86	2.86					
NO, MLB/HR	1.18	1.18	0.05	0.05	0.05					
TOTAL GAS, MLB/HR	2358.48	2341.42	99.45	99.45	116.51					
Fe_2O_3, MLB/HR						0.02256	43.89	43.89	32.48	32.48
$Fe_2(SO_4)_3$, MLB/HR							3.17	3.17	31.66	31.66
TOTAL SOLID, MLB/HR						0.02256	47.06	47.06	64.14	64.14
ENTHALPY, MM BTU/HR	360.26	358.36	-	28.64	32.85	-	10.67	5.52	7.71	15.08

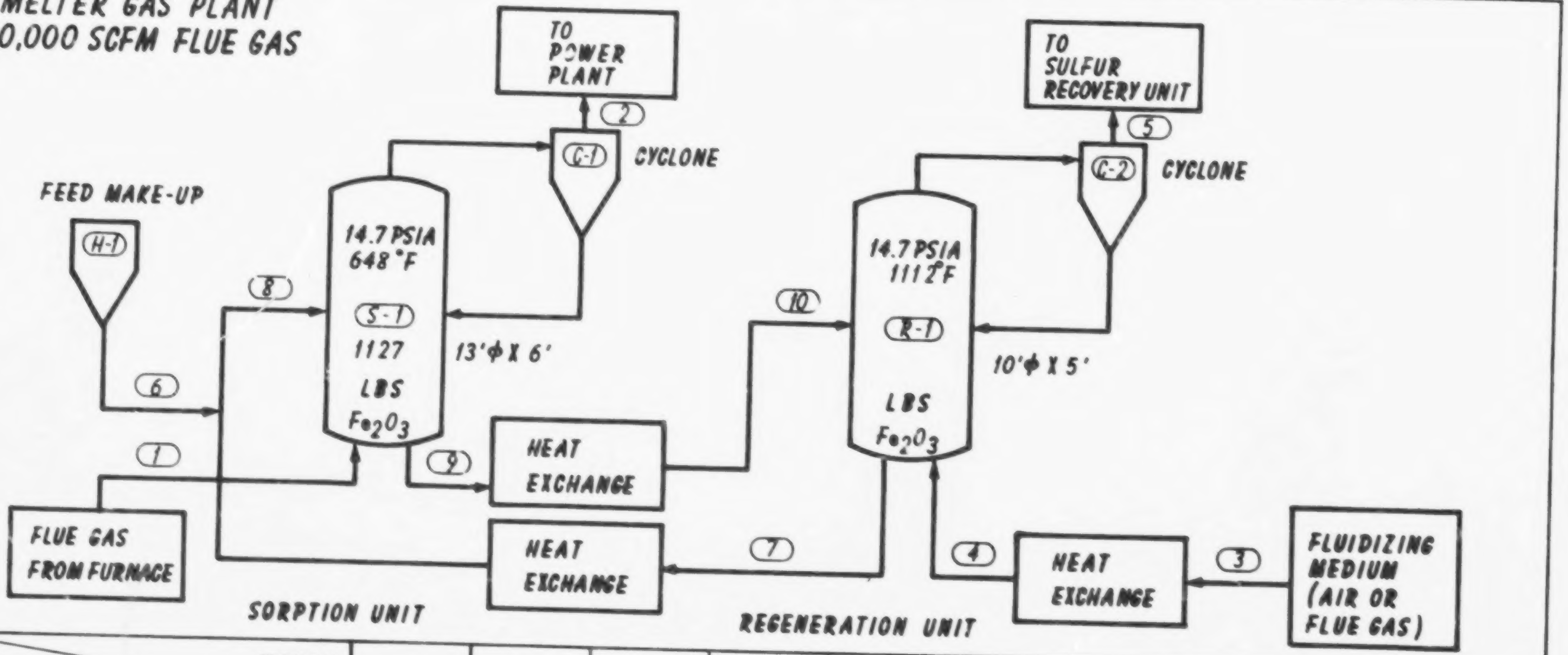
M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

TRACOR
AUSTIN TEXAS

PROCESS FLOWSHEET DATE - JUNE 30, 1969

A6-164-37

SMELTER GAS PLANT
20,000 SCFM FLUE GAS


TO POWER PLANT
2
C-1
CYCLONE
TO SULFUR RECOVERY UNIT
5
C-2
CYCLONE
FEED MAKE-UP
H-1
8
14.7 PSIA
648°F
S-1
1127
LBS
Fe_2O_3
13'φ X 6'
6
1
9
HEAT EXCHANGE
FLUE GAS FROM FURNACE
HEAT EXCHANGE
10
14.7 PSIA
1112°F
R-1
LBS
Fe_2O_3
10'φ X 5'
7
4
HEAT EXCHANGE
3
FLUIDIZING MEDIUM (AIR OR FLUE GAS)
SORPTION UNIT
REGENERATION UNIT

COMPONENT / STREAM	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
SO_2, MLB/HR	5.87	0.97	0.38	0.38	0.38					
SO_3, MLB/HR	-	-	-	-	6.12					
N_2, MLB/HR	71.15	71.15	27.97	27.97	27.97					
CO_2, MLB/HR	2.36	2.36	0.93	0.93	0.93					
H_2O, MLB/HR	0.06	0.06	0.02	0.02	0.02					
O_2, MLB/HR	14.46	13.24	5.20	5.20	5.20					
CO, MLB/HR	0.53	0.53	0.21	0.21	0.21					
TOTAL GAS, MLB/HR	94.43	88.31	34.71	34.71	40.83					
Fe_2O_3, MLB/HR						0.00810	15.71	15.71	11.69	11.69
$Fe_2(SO_4)_3$, MLB/HR							1.13	1.13	11.27	11.27
TOTAL SOLID, MLB/HR						0.00810	16.84	16.84	22.96	22.96
ENTHALPY, MM BTU/HR	13.66	12.97	-	9.47	10.97	-	3.84	1.99	2.76	5.40

M = 1000
MM = 1,000,000
ENTHALPY DATUM - 60°F

TRACOR™
AUSTIN TEXAS

PROCESS FLOWSHEET

DATE - JUNE 30, 1969

A6-164-37

8.3 REFERENCES USED IN WRITING TECHNICAL MEMORANDUMS

AD-001	L. H. ADAMI, E. G. KING, U. S. BUR. MINES, REPT. OF INVEST. NO. 6617, (1965).
AL-001	ALBERT AND SCHULZ, DEUTSCHES REICHS PATENT 238361 (1910).
AM-001	AMERICAN PETROLEUM INSTITUTE STANDARD 650, THIRD EDITION, AMERICAN PETROLEUM INSTITUTE. DIVISION OF REFINING, 1271 AVE. OF AMERICAS, NEW YORK, NEW YORK.(JULY,1966).
AN-001	H. W. ANDERSON, L. BROMLEY, J. PHYS. CHEM., VOL. 63, P. 1115, (1959).
AR-001	P. S. APIES, R. D. NEWTON, CHEMICAL ENGINEERING COST ESTIMATION, MCGRAW-HILL, NEW YORK, (1955).
AS-001	ASKENASY AND KLONOWSKY, Z. ELEKTROCHEM., VOL. 16, P. 104 (1910).
BA-001	R. F. BARROW, ET. AL., TRANS. FAR. SOC., VOL. 51, P. 1480, (1955).
BA-002	BADISCHE ANILIN UND SODA FABRIK, DEUTSCHES REICHS PATENT 291792.
BA-003	BADISCHE ANILIN UND SODA FABRIK, DEUTSCHES REICHS PATENT 283824
BA-004	D. BALAREW, Z. ANORG. ALLGEM. CHEM., VOL. 134, P. 77 (1914).
BE-001	F. BENTON, J. AM. CHEM. SOC., VOL. 45, P.900 (1923).
BE-002	BERTHELOT, ESSAI DE MECANIQUE CHIMIQUE, PART 1, P. 319.
BI-001	W. BILTZ, Z. ELEKTROCHEM., VOL. 37, P. 498 (1931).
BI-002	W. BILTZ, Z. ANORG. CHEM., VOL. 71, P. 427 (1911).
BI-003	W. BILTZ, ET. AL., Z. ANORG. CHEM., VOL. 233, P. 257 (1937).

BI-004 W. BILTZ, H. MULLER, Z. ANORG. ALLGEM. CHEM., VOL. 163, P. 257 (1927).

BI-005 W. BILTZ, H. MULLER, Z. ANORG. ALLGEM. CHEM., VOL. 163, P.295 (1927).

BO-001 J. BOUSQUET, G. PERACHON, COMPT. REND., VOL. 258, NO. 15, P. 3869 (1964).

BO-002 BOERICKE AND BANGERT, U. S. BUREAU OF MINES, REPT. OF INVEST. NO. 3813 (1945).

BR-001 L. BREWER, CHEMICAL REVIEWS, VOL. 52, P. 1 (1953).

BR-002 BRITZKE AND KAPUSTINSKII, Z. ANORG. CHEM., VOL. 194, P. 323, (1930).

BR-003 BRITZKE AND KAPUSTINSKII, J. PHYS. CHEM. (USSR), VOL. 5, P. 65, (1934).

BR-004 L. BREWER, L. BROMLEY, THE CHEMISTRY AND METALLURGY OF MISCELLANEOUS MATERIALS, (1950).

BR-005 D. BRADLEY, THE HYDROCYCLONE, PERGAMON PRESS, NEW YORK (1965).

BR-006 S. BRUNAUER, P.H. EMMETT, T. TELLER, J. AM. CHEM. SOC., VOL. 60, P. 309 (1938).

CA-001 CHEMICAL ABSTRACTS,64:3336A. A.A. SHIDLOVSKII, A.A. VOSKRESENSKII. ZH. FIZ. KHIM. VOL. 39, PP. 3097-9(1965).

CA-002 CHEMICAL ABSTRACTS,64:7434D. T.R. INGRAHAM, P. MARIER. CAN. MET. QUART VOL. 4, PP. 169-76(1965).

CA-003 CHEMICAL ABSTRACTS,52:70E. N.A. LANDIYA, T. GRUZIN. POLITEKH. INST. PP. 43-9(1953).

CA-004 CHEMICAL ABSTRACTS,58:7432D A.A. FOTIEV. ZH. PRIKL. KHIM. VOL. 35, PP. 2402-9(1962).

CA-005	CHEMICAL ABSTRACTS,64:11950F. I.J.BEAR, A.G. TURNBULL, J. PHYS. CHEM. VOL. 70, PP. 711-17(1966).
CA-006	CHEMICAL ABSTRACTS,59:13403G. A.A. SHIDLOVSKII, A.A. VOSKRESENSKII. ZH. FIZ. KHIM. VOL. 37, PP. 2062-7(1963).
CA-007	CHEMICAL ABSTRACTS,65:19366F. G. V. FIDLIDER, ET AL. ZH. FIZ. KHIM. VOL. 40, PP. 2168-70(1966).
CA-008	CHEMICAL ABSTRACTS,54:6287A. H.W. GOLDSTEIN, ET AL. J. PHYS.CHEM. VOL. 63, PP. 1445-9(1959).
CA-009	CHEMICAL ABSTRACTS 64:1418G. R. BARANY, L.H. ADAMI, U. S. BUR. MINES, REPT. INVEST. NO. 6687(1965).
CA-010	CHEMICAL ABSTRACTS,65:3094B. E.A. GORGORAKI, V.V. TARASOV. TR. MOSK. KHIM.-TEKHNOL. INST. NO. 49, PP. 11-15(1965).
CA-011	CHEMICAL ABSTRACTS 54:19142C. S.W. MAYER, ET AL. J. PHYS. CHEM. VOL. 64, PP. 911-14 (1960). SEE TR-005 AND TR-006.
CA-012	CHEMICAL ABSTRACTS,64:4343A. M.A. GREENBAUM, ET AL. J. PHYS. CHEM. VOL. 69, PP. 4035-7(1965).
CA-013	CHEMICAL ABSTRACTS 65:17802F. H.BREKKEN. J. APPL. PHYS. VOL. 37, PP. 3635-6 (1966).
CA-014	CHEMICAL ABSTRACTS, 59:5860A W.W. WELLER, E.G. KING. U.S. BUR. MINES, REPT. INVEST. NO. 6245 (1963).
CA-015	CHEMICAL ABSTRACTS 55:3023B. YA. I. GERASIMOV, ET AL. DOKL. AKAD. NAUK SSSR VOL. 134, PP. 1350-2(1960).
CA-016	CHEMICAL ABSTRACTS 58:14875H. W.E. BELL, M. TAGAMI, J. PHYS. CHEM. VOL. 67, PP. 2432-6 (1963).

CA-017	CHEMICAL ABSTRACTS 58:6257F. W.W. WELLER, E.G. KING U. S. BUR. MINES, REPT. INVEST. NO. 6147 (1963) .
CA-018	CHEMICAL ABSTRACTS,58:2308C. F.A. KUZNETSOV, T.N. REZUKHINA. ZH. FIZ. KHIM. VOL. 35, PP. 956-7 (1961).
CA-019	CHEMICAL ABSTRACTS,54:21971G. W.W. WELLER, E.G. KING, U. S. BUR. MINES REPT. INVEST. NO. 5590 (1960).
CA-020	CHEMICAL ABSTRACTS 65:9827D. N.G. BARANCHEEVA , L.A. ZHARKOVA. ZH. FIZ KHIM.VOL. 40, PP. 1368-70 (1966).
CA-021	CHEMICAL ABSTRACTS 64:16722G V.A. LEVITSKII, ET AL. ELEKTROKHIMIYA. VOL. 1, PP. 1371-4 (1965).
CA-022	CHEMICAL ABSTRACTS 54:17023G. C. BRISI, F. ABBATTISTA. ANN. CHIM. (ROME) VOL. 50, PP.165-8(1960). SEE TR-005
CA-023	CHEMICAL ABSTRACTS 59:7028H. V. A. LEVITSKII, T. N. REZUKHIMA. ZH. FIZ KHIM.VOL. 37, PP. 1135-7 (1963). SEE TR-005.
CA-024	CHEMICAL ABSTRACTS 61:1321E. L.A.ZHARKOVA, N.G. BARANCHEEVA. ZH. FIZ. KHIM. VOL. 38, PP. 752-4 (1964).
CA-025	CHEMICAL ABSTRACTS 65:95D. V.A. LEVITSKII, ET AL. IZV. AKAD.NAUK SSSR NEORGAN. MATERIALY. VOL. 2, PP. 325-31 (1966). SEE TR-005.
CA-026	CHEMICAL ABSTRACTS 56:13628A. F. MASSAZZA, ANN. CHIM. (ROME) VOL. 52, PP. 51-8.
CA-027	CHEMICAL ABSTRACTS 65:3822G. L.M. LENEV, I.A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, METALLY, PP. 73-8, (1966). SEE TR-005
CA-028	CHEMICAL ABSTRACTS 65: 9831C. M. FISCHER. Z. ANORG. ALLGEM. CHEM. VOL. 345, PP. 134-5 (1966).

CA-029 CHEMICAL ABSTRACTS 63:1265F. R. BARANY. U. S. BUR. MINES, REPT. INVEST
NO. 6618, (1965). SEE TR-005.

CA-030 CHEMICAL ABSTRACTS 56:2046C. Z.V. PROSHINA, T.N. REZUKHINA. ZHUR.
NEORGAN. KHIM. VOL. 5, PP. 1015-21 (1960). SEE TR-005

CA-031 CHEMICAL ABSTRACTS 61:12705E. L. M. LENEV, I. A. NOVOKHATSKII. IZV.
AKAD. NAUK SSSR, MET. I GORN. DELO, PP. 87-90 (1964) SEE TR-005.

CA-032 CHEMICAL ABSTRACTS 59:76F. T. N. REZUKHINA, V. A. LEVITSKII. ZH. FIZ.
KHIM. VOL. 37, PP. 667-8 (1963) SEE TR-005.

CA-033 CHEMICAL ABSTRACTS 63:5007D A.N. GOLUBENKO, ET AL. ZH. FIZ. KHIM. VOL.
39, PP. 1164-7 (1965).

CA-034 CHEMICAL ABSTRACTS 63:7701D. V. A. LEVITSKII, ET AL. ELEKTROKHIMIYA
VOL. 1, PP. 237-9 (1965). SEE TR-005.

CA-035 CHEMICAL ABSTRACTS 63:7701G. A. N. GOLUBENKO, T. N. REZUKHINA. ZH.
FIZ. KHIM. VOL. 39, PP. 1519-21 (1965) SEE TR-005.

CA-036 CHEMICAL ABSTRACTS 63:6389D. Y. A. ZAIONCHKOVSKII, E. V. RUBAL'SKAYA.
IZV. AKAD. NAUK SSSR, NEORGAN. MATERIALY. VOL. 1, PP. 257-9 (1965).

CA-037 CHEMICAL ABSTRACTS 64:1415A. L. M. LENEV, I. A. NOVOKHATSKII. ZH.
NEORGAN. KHIM. VOL. 10, PP. 2400-3 (1965) SEE TR-005.

CA-038 CHEMICAL ABSTRACTS 59:2473D. I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR
OTD. TEKHN. NAUK, MET. I GORN. DELO 1963.

CA-039 CHEMICAL ABSTRACTS 62:9867H. B. I. PANFILOV, N. N. FEODOS'EV. ZH
NEORGAN. KHIM. VOL. 10 PP. 298-9 (1965). SEE TR-005.

CA-040 CHEMICAL ABSTRACTS 63:2389E. L. A. ZHARKOVA, ET AL. DOKL. AKAD. NAUK
SSSR. VOL. 128, PP. 992-4 (1959).

CA-041	CHEMICAL ABSTRACTS 55:7022H. M. KOEHLER, U.S. BUR. MINES, REPT. INVEST NO. 5700, (1960). SEE TR-005.
CA-042	CHEMICAL ABSTRACTS 55:11057C. L. A. REZNITSKII, K.G.KHOMYAKOV. DOKL. AKAD. NAUK SSSR. VOL. 31, PP. 325-6(1960). SEE TR-005.
CA-043	CHEMICAL ABSTRACTS 56:15000H. A. S. BEREZHONI, DOPOVIDI AKAD. NAUK UKR. RSR, PP. 55-8 (1962). SEE TR-005.
CA-044	CHEMICAL ABSTRACTS 59:2387E. T. N. REZUKHINA, V. A. LEVITSKII. ZH. FIZ KHIM. VOL. 37, PP. 2357-60 (1963) SEE TR-005.
CA-045	CHEMICAL ABSTRACTS 57:2327E. R. BARANY, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 5973 (1962). SEE TR-005.
CA-046	CHEMICAL ABSTRACTS 58:13212B. W. W. WELLER, K.K. KELLEY U. S. BUR. MINE REPT. INVEST. NO. 6191 (1963).
CA-047	CHEMICAL ABSTRACTS 57:13233C. L.A. REZNITSKII, K. G. KHOMYAKOV. VESTN. MOSK. UNIV., SER. II, KHIM. VOL. 15, PP. 28-30(1960) SEE TR-005.
CA-048	CHEMICAL ABSTRACTS 62:4696D. R. L. ALTMAN, J. PHYS. CHEM. VOL. 68 PP. 3425-6 (1964). SEE TR-005.
CA-049	CHEMICAL ABSTRACTS 64:7435D. O. J. KLEPPA, A. NAVROTSKY. INORGAN. CHEM. VOL 5, PP. 192-3 (1966) SEE TR-005.
CA-050	CHEMICAL ABSTRACTS 57:15893G. E. G. KING, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 6049 (1962) SEE TR-005.
CA-051	CHEMICAL ABSTRACTS 58:5103C. W. W. WELLER, E. G. KING, U.S. BUR. MINE REPT. INVEST. NO. 6130 (1962). SEE TR-005.
CA-052	CHEMICAL ABSTRACTS 55:10993H. W.W. WELLER, E. G. KING. U. S. BUR. MINES, REPT. INVEST. NO. 5954 (1961) .

CA-053	CHEMICAL ABSTRACTS 62:12509H. A.N. GOLUBENKO, T. N. REZUKHINA. ZH. FIZ KHIM. VOL. 38, PP. 2920-3 (1954).
CA-054	CHEMICAL ABSTRACTS 61:5277C. L. M. LENEV, I. A. NOVOKHATSKII. IZV. AKAD. NAUK SSSR, MET. I GORN. DELO PP. 47-51 (1963). SEE TR-005
CA-055	CHEMICAL ABSTRACTS 64:7432G. I. A. NOVOKHATSKII, L. M. LENEV. IZV. VYSSHIKH. UCHEBN. ZAVEDENII, TSVETN. MET. VOL. 8 PP. 68-74. SEE TR-005
CA-056	CHEMICAL ABSTRACTS 66:33118C.N. A. LANDIYA, ET AL. IZV. AKAD. NAUK SSSR, NEORG. MATER. VOL. 2 , PP. 2050-7 (1966).
CA-057	CHEMICAL ABSTRACTS 66:69464J. D. BHOGESWARA RAO, V.V. DADAPE. J. PHYS. CHEM., VOL. 71, PP. 537-40 (1967). SEE TR-005.
CA-058	CHEMICAL ABSTRACTS 48:7419G. KUAN PAN J. CHINESE CHEM. SOC. (TAIWAN) SER II. VOL. 1, PP. 1-15 (1954).
CA-059	CHEMICAL ABSTRACTS 48:1131F. E.J. HUBER, C.E. HOLLEY J. AMER. CHEM. SOC. VOL. 75, PP. 3594-5 (1953).
CA-060	CHEMICAL ABSTRACTS 57:2327F. A. D. MAH U. S. BUR. MINES, REPT. INVEST. NO. 5972 (1962).
CA-061	CHEMICAL ABSTRACTS 56:13628A. F. MASSAZZA. ANN. CHIM. (ROME) VOL. 52, PP. 51-8 (1962).
CA-062	CHEMICAL ABSTRACTS 61:11662F. W. W. WELLER, ET AL. U. S. BUR. MINES, REPT. INVEST. NO. 6513 (1964).
CA-063	CHEMICAL ABSTRACTS 63:14148H. B. I. PANFILOV, N. N. FEODOS'EV, ZH. NEORGAN. KHIM. VOL. 10, PP. 1344-7 (1965).
CA-064	CHEMICAL ABSTRACTS 65:6386H. W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 6782 (1966).

CA-065 CHEMICAL ABSTRACTS 66:89119D. O. J. KLEPPA, ACTA. CHEM. SCAND. VOL. 20, PP. 2568-72 (1966).

CA-066 CHEMICAL ABSTRACTS 56:1003H. E. F. WESTRUM, A. F. BEALE, J. PHYS. CHEM. VOL. 65, PP. 353-5 (1961).

CA-067 CHEMICAL ABSTRACTS 58:60H. E. H. P. CORDFUNKE, G. MEYER, REC. TRAV. CHIM., VOL. 81, PP. 670-8 (1962).

CA-068 CHEMICAL ABSTRACTS 63:9122G. T. N. REZUKHINA, ET.AL., ELEKTROKHIMIYA VOL.1, PP.467-71 (1965). SEE TR-005.

CA-069 CHEMICAL ABSTRACTS 54:17028F. L. G. HEPLER, ET AL., J. PHYS. CHEM., VOL. 64, PP9 375-7 (1960).

CA-070 CHEMICAL ABSTRACTS,54:10465F. E.ERDOS, ET AL. COLL. CZECH. CHEM. COMMUN., VOL.24, PP. 3836-43(1959).

CA-071 CHEMICAL ABSTRACTS,54:14904E. K.M.KOLBINA, ET AL. VESTNIK LENINGRAD UNIV., VOL.15, SER. KHIM. I FIZ., PP. 122-9(1960).

CA-072 CHEMICAL ABSTRACTS,61:7771G. G.A. BERGMAN, E.I.SCHMUK, IZV. AKAD. NAUK SSSR MET. I GORN. DELO, NO.3, PP.91-9(1964).

CA-073 CHEMICAL ABSTRACTS,57:13234C. W.W.WELLER, E.G.KING, U.S. BUR. MINES, REPT. INVEST. NO 6040 (1962).

CA-074 CHEMICAL ABSTRACTS,57:2927G. J.W.COBBLE,J.E.MCDONALD, J. PHYS. CHEM., VOL.66, P.731(1962).

CA-075 CHEMICAL ABSTRACTS,57:394C. E.D.CATER, ET AL. J. CHEM. PHYS., VOL. 35, PP. 608-18 (1961).

CA-076 CHEMICAL ABSTRACTS,58:8459B. T.N. REZUKHINA, ET AL, ZH. FIZ. KHIM., VOL. 35, PP.2539-42 (1961).

CA-077 CHEMICAL ABSTRACTS,58:5100C. R. BARANY, U. S. BUR. MINES, REPT. INVEST. NO 6143 (1962).

CA-078 CHEMICAL ABSTRACTS,55:8026C. L. REZNITSKII, K.G.KHOMYAKOV, VESTNIK MOSKOV. UNIV., SER. II, VOL.15, PP. 40-2 (1960).

CA-079 CHEMICAL ABSTRACTS,66:89104V. M.G. ZURALEVA, MATER. NAUCH. KONF. SOVNAR. NIZHNEV. EKON. RAIONA, VOLG. POLI. INST., VOL.2,PP235-9(1965).

CA-080 CHEMICAL ABSTRACTS,68:69331Z. A.A.SHIDLOVSKII, A.A.VOSKRESENSKII, ZH. FIZ. KHIM., VOL.41, PP.1246-7 (1967).

CA-081 CHEMICAL ABSTRACTS,59:1256B. H. SCHAEFER, ET AL., Z. ANORG. ALLG. CHEM., VOL. 321, PP. 41-55 (1963).

CA-082 CHEMICAL ABSTRACTS,58:7566F. H. SCHAEFER,ET AL. Z. ANORG. ALLGEM. CHEM., VOL 319, PP. 327-35(1963).

CA-083 CHEMICAL ABSTRACTS,55:7023A. S.A. SHCHUKAREV, A.N. RYABOV, ZHUR. NEORG. KHIM., VOL. 5, PP.1931-3 (1960).

CA-084 CHEMICAL ABSTRACTS,61:12709B. K.K. KELLEY, W. W. WELLER, U. S. BUR. MINES, REPT. INVEST. NO. 6511 (1964).

CA-085 CHEMICAL ABSTRACTS,56:12374E. T. N. REZUKHINA, ET AL., DOKL. AKAD. NAUK SSSR, VOL. 139, PP. 1405-6, (1961).

CH-001 J. CHIPMAN, J. AM. CHEM. SOC., VOL. 83, P. 1762 (1961).

CH-002 J. CHIPMAN, H. M. CHAN, TRANS. AMER. SOC. METALS, VOL. 38, P. 70 (1947).

CL-001 A. CLERICI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI SCANDIO, ITTRIO, LANTANIO, NEODIMIO, SAMARIO,' GAZZ. CHIM. ITAL., VOL. 93, PP. 1444-54 (1963).

CO-001 J.P. COUGHLIN, CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY, U. S. BUR. MINES BULL. 542 (1954).

CO-002 COURTOIS AND GASTEN, COMPT. REND., VOL. 207, P. 1220 (1938).

CO-003 M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI LANTANIO E SAMARIO,' GAZZ. CHIM. ITAL., VOL. 92, PP.447-53(1962).

CO-004 M. COLA, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI ALCUNI SOLFITI METALLICI,' GAZZ. CHIM. ITAL., VOL. 91, PP. 173-86 (1961).

CO-005 M. COLA, C. CASTELLANI BISI, S. TARANTINO, GAZZ. CHIM. ITAL., VOL. 91, P. 105 (1961).

DA-001 D'ANS, DISSERTATION DARMSTADT, P. 48 (1905).

DE-001 DEUTSCHES REICHS PATENT 106715, 107995, 108445, 108446.

DE-002 DEUTSCHES REICHS PATENT 310070.

DE-003 DEUTSCHES REICHS PATENT 297922.

DE-004 DEUTSCHES REICHS PATENT 339611.

DE-005 DEUTSCHES RETCHS PATENT 347694.

DI-001 P. V. DIBINA, 'THERMAL STABILITY OF ALUMINUM SULFITES,' KHIM. AND KHIM. TEKH., NO. 5, PP. 902-7 (1960).

DR-001 N. DROZIN, RUSS. J. PHYS. CHEM., VOL. 38, P. 1386 (1964).

DW-001 A.S.DWORKIN, M.A.BREDIG, J. PHYS. CHEM., VOL.72, PP.1277-81(1968).

EL-001 J.F. ELIOTT, M. GLEISER, THERMOCHEMISTRY FOR STEELMAKING, ADDISON-WESLEY PUBLISHING CO., INC., READING, MASS.

ER-001	E. ERDOS. THERMODYNAM. PROP. OF SULFITES,FIRST COMMUN. IN 'COLLECTION CZECHOSLOV. CHEM. COMMUN.,PRAGUE,VOL.27,PP.1426,1437(1962).
ER-002	E. ERDOS. THERMODYNAM. PROP. OF SULFITES,SEC. COMMUN. IN 'COLLECTION CZECHOSLOV. CHEM. COMMUN.,PRAGUE,VOL.27,PP.2273-2283(1962).
ER-003	E. ERDOS, 'EQUILIBRIA IN THE SYSTEMS SO2-CO2-MO,' COLL. CZECH. CHEM. COMMUN., VOL. 27, P. 2152-67 (1962).
EU-001	A. EUCKEN, LEHRBUCH DER CHEM. PHYS., LEIPZIG,(1930),P.627.
FA-001	FARBENFABRIKEN FR. BAYER AND CO., DEUTSCHES REICHS PATENT 280960, 1912
FI-001	FIRMA DE HAEN, DEUTSCHES REICHS PATENT 128616 (1900).
FI-002	FIRMA PINTSCH, ENGLISH PATENT 5025 (1912).
FI-003	G. FITTERER, 'PROCEEDINGS OF THE FIRST INTERNATIONAL MEETING ON APPLICATIONS OF FUNDAMENTAL THERMODYNAMICS TO METALLURGICAL PROCESSES', GORDON AND BREACH, NEW YORK (U967).
FL-001	H. FLOOD, O.J. KLEPPA. J. AMER. CHEM. SOC. VOL. 69, PP. 998-1002 (1947) .
FO-001	F. FOERSTER, K. KUBEL, 'ZERSETZUNG DER SCHWEFLIGSAUREN SALZE IN DER GLUHITZE,' Z. ANORG. CHEM., VOL 139, PP. 261-92 (1924).
FO-002	V. FOMIN, ZH. FIZ. KHIM., VOL. 27, P. 1689 (1953).
FR-001	FRICKE AND DONGES, Z. ANORG. CHEM., VOL. 250, P. 202 (1942).
FR-002	J. FRAZER, 'MANGANESE DIOXIDE IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE,' J. AM. CHEM. SOC., VOL. 45, P.2841(1923).
FR-003	J. FRAZER, 'THE CATALYTIC OXIDATION OF CARBON MONOXIDE,' J. PHYS. CHEM., VOL. 35, P. 405 (1931).

GA-001 E. RES. GARRINI, C. CASTELLANI BISI, 'DECOMPOSIZIONE TERMICA DI SOLFITI DI POTASSIO, LITIO,E AMMONIO,' GAZZ. CHIM ITAL., VOL. 93, PP. 1252-8 (1963).

GI-001 A.M. GINSTLING, M.D. VOLKOV, ZHUR. PRIKL. KHIM., VOL. 33, NO. 8, PP. 1700-4 (1960).

GM-001 L. GMELIN, GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE, SULFUR, PART A PP. 324-51 (1953).

GO-001 W. D. GOOD, J. PHYS. CHEM., VOL. 66, P. 380 (1962).

GO-002 M. GOLDSCHMIDT, L. THOMASSEN, VID. SELSKP. SKR. I, MATH. NAT. KLASSE (1923), NO. 2.

GR-001 R. C. GRIFFIS, J. ELECTROCHEM. SOC., VOL. 106, P. 418 (1959).

GR-002 S. J. GREGG, K. S. W. SING, ADSORPTION, SURFACE AREA AND POROSITY, ACADEMIC PRESS, NEW YORK (1967)

GR-003 S.J. GREGG, 'THE SURFACE CHEMISTRY OF SOLIDS', SECOND EDITION, REINHOLD PUBLISHING CORP., NEW YORK (1961).

HA-001 HAMMICK, J. CHEM. SOC. , III, P. 381, (1917).

HA-002 W. E. HAND, 'FROM FLOW SHEET TO COST ESTIMATE', PETROLEUM REFINER, VOL. 37, NO. 9, PP. 331-4, (1958).

HE-001 L. G. HEPLER, R. L. GRAHAM J. AMER. CHEM. SOC. VOL. 80, PP. 3538-40 (1958).

HE-002 L.G.HEPLER, R.N.GOLDBERG, CHEM. REVIEWS, VOL. 68, PP. 229-52(1968).

HE-003 L. G. HEPLER, C. N. MULDROW, J. PHYS. CHEM., VOL.62, P. 982 (1958).

HI-001 C. HIRAYAMA, J. CHEM. ENG. DATA, VOL. 9, P. 65 (1964).

HO-001	H. N. HOLMES. A. L. ELDER, IND. ENG. CHEM., VOL. 22, P. 471 (1930).
HO-002	R. HOPPE, Z. ANORG. ALLGEM. CHEM., VOL. 296, P. 104 (1958).
HO-003	W. HOLLOWAY, GRAVER TANK COMPANY, HOUSTON, TEXAS, PRIVATE COMMUNICATION OF 27 JANUARY,1963.
HU-001	E.J. HUBER, C.E. HOLLEY, J. AM. CHEM. SOC., VOL. 75, P. 3594, (1953).
HU-002	G.L. HUMPHREY, J. AM. CHEM. SOC., VOL. 76, P. 978 (1954).
HU-003	E. J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 793 (1963).
HU-004	E.J. HUBER, C. HOLLEY, J. PHYS. CHEM., VOL. 67, P. 1731 (1963).
HU-006	E.J. HUBER, C. HOLLEY, J. CHEM. ENG. DATA, VOL. 13, P. 252 (1968).
HU-007	G. L. HUMPHREY, J. AM. CHEM. SOC., VOL. 75, P. 2806 (1953).
HU-008	E.J. HUBER, C. HOLLEY, J. AM. CHEM. SOC., VOL. 77, P. 1444 (1955).
HU-009	HUTTIG AND SCHRODER, Z. ANORG. ALLGEM. CHEM., VOL. 121, P.243 (1922).
IN-001	T.R. INGRAHAM. TRANS. MET. SOC. AIME VOL. 227 PP.1419-26(1963). SEE TR-005 AND TR-006
IN-002	T.R. INGRAHAM. TRANS. MET. SOC. AIME VOL. 233, PP.359-63(1965). SEE TR-005 AND TR-006
IN-003	T.R. INGRAHAM, PROCEEDINGS OF FIRST TORONTO SYMPOSIUM ON THERMAL ANALYSIS, PP. 31-33, H.G. MCADIE, ED., TORONTO SECTION, CHEM. INST. OF CANADA, FEB. 8, 1965.
IN-004	T.R. INGRAHAM, A.N. WARNER, CAN. J. CHEM., VOL. 38, PP. 2196-202 (1960).

IN-005 T.R. INGRAHAM, CAN. MET. QUART., VOL. 3, NO. 3, PP. 220-34 (1964).

IN-006 T.R. INGRAHAM, CAN. MET. QUART., VOL. 5, PP. 109-22 (1966).

IN-007 T.R. INGRAHAM, TRANS. MET. SOC. AIME, VOL. 236, NO. 7, PP. 1064-7 (1966).

JA-001 JANAF THERMOCHEMICAL TABLES,THE DOW CHEMICAL CO.,MIDLAND,MICHIGAN, AUG.,1965.

JE-001 K. JELLINEK, J. ZAKOWSKII, Z. ANORG. CHEM., VOL. 142, PP.1-53, (1925).

JO-001 H.L. JOHNSTON, ET. AL., J. AM. CHEM. SOC., VOL. 73, P. 1112, (1951).

JU-001 JUZA AND MEYER, Z. ANORG. CHEM., VOL. 213, P. 273 (1933).

KA-001 KAPUSTINSKII AND GOLUTWIN, IZVEST. AKAD. NAUK SSSR, OTDEL KHIM. NAUK, P. 192 (1951).

KA-002 M. KARAPET'YANTS, ZH. FIZ. KHIM., VOL. 30, P. 593 (1956).

KA-003 A. F. KAPUSTINSKII, O. SAMOILOV, IZV. AKAD. NAUK SSSR, OTD. KHIM. NAUK, P. 337-43 (1950). CHEM. ABSTRACTS,44:9790F.

KA-004 K. KATO, C. Y. YEN, 'BUBBLE ASSEMBLAGE MODEL FOR FLUIDIZED BED CATALYTIC REACTORS,' OFFICE OF COAL RESEARCH, PAPER NO. VIII, CONTRACT 14-01-0001-497, (SEPTEMBER, 1968).

KE-001 K.K. KELLEY. CALCULATION OF THERMOCHEMICAL PROPERTIES IN 'JANAF THERMOCHEMICAL TABLES,DOW CHEM. CO.,MIDLAND,MICH.,AUG.,1965.

KE-002 K.K. KELLEY. CONTRIBUTIONS TO DATA ON THEORETICAL METALLURGY U. S. BUREAU OF MINES, BULLETIN 584(1960).

KE-003 H.H. KELLOG. TRANS. MET. SOC. AIME VOL. 218, PP. 70-81 (1960). SEE TR-005.

KE-004 K. K. KELLEY, W. W. WELLER, J. S. BUR. MINES, REPT. INVEST. NO. 5984 (1962).

KE-005 K. K. KELLEY, CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY, U.S. BUREAU OF MINES BULLETIN 406, (1937).

KE-006 A. KETOV, V. PECHKOVSKII, 'STUDY OF THE THERMAL DECOMPOSITION OF MAGNESIUM SULFITE,' RUSS. J. INORG. CHEM., VOL.4, PP.118-20 (1959).

KE-007 KEPPELER, Z. ANGEW. CHEM., VOL. 21, PP. 552-77 (1908).

KE-008 K. K. KELLEY, THE ENTROPIES OF INORGANIC SUBSTANCES: REVISION OF DATA, U. S. BUREAU OF MINES BULL. 477(1950).

KI-001 W. A. KIREJEW, J. CHIM. GEN. (USSR), VOL. 16, P. 1569, (1946).

KI-002 E. G. KING, W. W. WELLER, U. S. BUR. MINES, REPT. OF INVEST. NO. 5791 (1961).

KL-001 KLEMM AND SCHNICK, Z. ANORG. CHEM., VOL. 226, P. 353 (1936).

KO-001 KORSHUNOV, J. PHYS. CHEM.(U.S.S.R.), VOL. 13, P. 703 (1939).

KR-001 D. H. KRIKORIAN, J. PHYS. CHEM., VOL. 67, PP. 1586-9 (1963).

KR-002 KRAUS AND RIDDERHOFF, J. AM. CHEM. SOC., VOL. 56, P. 79 (1934).

KR-003 C. KROGER, 'ZUR HETEROGENEN KATALYSE BINARER GASREAKTIONEN,' Z. ANORG. CHEM., VOL. 205, PP. 369-97 (1932).

KU-001 O. KUBASCHEWSKI, ET AL . METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS 4TH EDITION (1967).

KU-002 O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS, (1959).

KU-003 O. KUBASCHEWSKI , THERMO. DATA OF THE ALLOYS, PERGAMON PRESS, (1956).

KU-004 KUBASCHEWSKI AND WEIBKE, THERMOCHEMIE DER LEGIERINGEN, SPRINGER, BERLIN, 1943.

KU-005 O. KUBASCHEWSKI , ET. AL., METALLURGICAL THERMOCHEMISTRY, PERGAMON PRESS, (1951).

KU-006 KUHLMANN, DEUTSCHES REICHS PATENT 406864.

KU-007 D. KUNII, O. LEVENSPIEL, 'BUBBLING BED MODEL FOR KINETIC PROCESSES IN FLUIDIZED BEDS,' I & E C PROCESS DESIGN AND DEVELOPMENT, VOL. 7, NO. 4, PP. 481-91 (OCT. 1968).

KU-008 D. KUNII, O. LEVENSPIEL, 'BUBBLING BED MODEL FOR THE FLOW OF GAS THROUGH A FLUIDIZED BED,' I & E C FUNDAMENTALS, VOL. 7, NO. 3 PP. 446-52 (AUG. 1968).

LA-001 KALORISCHE ZUSTANDGROESSEN IN 'LANDOLT BOERNSTEIN',SPRINGER-VERLAG, BERLIN,VOL.2,PART4(1961).

LA-002 W. LATIMER, J. AM. CHEM. SOC., VOL. 73, P. 1480 (1951).

LA-003 W. LATIMER, J. AM. CHEM. SOC., VOL. 43, P. 818 (1921).

LA-004 H. J. LANG, 'SIMPLIFIED APPROACH TO PRELIMINARY COST ESTIMATION', CHEMICAL ENGINEERING, JUNE (1948).

LE-001 LE BLANC, E. MOBIUS, Z. PHYS. CHEM., VOL. 142, P.151 (1929).

LE-002 LE BLANC AND SACHSE, Z. ELECTROCHEM., VOL. 32, P. 204 (1926).

LE-003 LEVITSKII, ET AL., RUSS. J. PHYS. CHEM., VOL. 35, NO. 6, P. 671 (1961)

LE-004 MAX LEVA, FLUIDIZATION, MCGRAW-HILL BOOK CO., NEW YORK, (1959).

LU-001 LUNGE AND POLLITT, Z. ANGEW. CHEM., VOL. 15, P.1105 (1902).

LU-002 LUNGE AND REINHARDT, Z. ANGEW. CHEM., VOL. 17, P. 1041 (1904).

MA-001 P. G.MASLOV. THERMODYNAM. CHARACTERISTICS OF CALCIUM, GALLIUM, INDIUM, AND THALLIUM COMPOUNDS. ZHUR. OBSCHCEIKHIM.,VOL.29,PP.1413-1423(1959).

MA-002 A. D. MAH, J. AM. CHEM. SOC., VOL. 81, P. 1582 (1959).

MA-003 A.D. MAH, U. S. BUR. MINES, REPORT OF INVESTIGATIONS NO. 5965, (1962).

MA-004 W. MACHU, METALL UND ERZ, VOL. 39, P. 495 (1938).

MA-005 MARCHAL, J. CHIM. PHYS., VOL. 23, P. 38, (1926).

MA-006 D. S. MACIVER, P. H. EMMETT, J. AM. CHEM. SOC., VOL. 60, P. 824 (1938).

ME-001 G. MEYER, E.H.P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 670, (1962).

ME-002 MEYER AND ROTGERS, Z. ANORG. ALLG. CHEM., VOL. 57, P. 104 (1908).

ME-003 G. MEYER, E. H. P. CORDFUNKE, REC. TRAV. CHIM., VOL. 81, P. 495 (1962).

MI-001 MIXTER, AM. J. SCI. , VOL. 28, P. 103 (1909).

MO-001 M. P. MOROZOVA, L. GETSKINA, VESTNIK LENINGRAD. UNIV., VOL. 14, NO. 22, SER. FIZ. I KHIM. NO. 4, VOL. 123, (1959).

MO-002	A. N. MOROZOVA, N. A. NOVOKHATSKII, IZV. A N SSSR, OTD. TEKHN. N., METALLURGIYA I TOPLIVO, NO. 6, P. 3 (1962).
NB-001	SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART I,NATIONAL BUREAU OF STANDARDS,1965.
NB-002	SELECTED VALUES OF CHEM. THERM. PROPERTIES.PART II,NATIONAL BUREAU OF STANDARDS,1966.
NB-003	F,ROSSINI,ET AL. SELECTED VALUES OF CHEM. THERM. PROPERTIES, NATL. BUREAU OF STANDARDS, CIRCULAR 500, (1952).
NB-004	NATIONAL STANDARD REFERENCE DATA SERIES NBS-7. HIGH TEMPERATURE PROPERTIES AND DECOMPOSITION OF INORGANIC SALTS. PART 1 SULFATES.
NB-005	SELECTED VALUES OF CHEM. THERM. PROPS., NATNL. BUR. STDS., TABLES FOR FIRST 34 ELEMENTS IN STD. ORDER OF ARRANGEMENT. TN 270-3 (1968).
NE-001	W. NERNST, LEHRBUCH DER PHYS. CHEM., 15TH EDITION, P. 766.
NE-002	B. NEUMAN, ET AL., 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCWEFELSAURE-KONTAKTPROZESS I.' Z. ELECTROCHEM, VOL. 34, PP. 696-734 (1928).
NE-003	B. NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE , VI.,' Z. ELECTROCHEM., VOL. 41, PP. 589-93 (1935).
NE-004	B. NEUMANN, E. GOEBEL, 'DIE WIRKSAMKEIT VERSCHIEDENER KONTAKTSUBSTANZEN BEIM SCHWEFELSAURE KONTAKTPROZESS II,' Z. ELECTROCHEM., VOL. 34, PP. 734-40 (1928).
NE-005	B. NEUMANN, E. GOEBEL, 'DIE ADSORPTION VON SCHWEFLIGER SAURE AN PLATIN, EISENOXYD UND CHROMOXYD, II.,' Z. ELECTROCHEM., VOL. 30, PP. 672-82 (1933).
NE-006	B.NEUMANN, 'ZUR SCHWEFELSAUREKATALYSE, V. ,' Z. ELEKTROCHEM., VOL. 38, PP. 304-11 (1932).

OL-001	C. R. OLSON, E. S. MCKELVY, 'HOW TO SPECIFY AND COST ESTIMATE ELECTRIC MOTORS,' HYDROCARBON PROCESSING, VOL. 46, NO. 10, PP. 117-34, (1967).
OR-001	M.H. ORTNER, J. CHEM. PHYS., VOL. 34, P. 556 (1961).
OW-001	B. OWENS, S. W. MAYER, J. INORG. NUCL. CHEM., VOL. 26, P. 501, (1964). SEE TR-005, TR-006.
OW-002	OWEN, J. AM. CHEM. SOC., VOL. 56, P. 1695 (1934).
PA-001	N.PARRAVANO, G.MALQUORI, ATTI. R. ACAD. LINCEI, SER. 6, VOL. 7, P. 189 (1928).
PA-002	PARRAVANO AND MALQUORI, ATTI. REND. ACCAD. LINCEI, SER. 6, VOL. 7, P. 109 (1929).
PA-003	GUY PANNETIER, 'DECOMPOSITION THERMIQUE DU SULFITE DE ZINC HYDRATE,' BULL. SOC. CHIM. FRANCE, VOL. 8, PP. 1949-56 (1964).
PA-004	L. PAULING, THE NATURE OF THE CHEMICAL BOND, CORNELL UNIVERSITY PRESS, ITHACA, NEW YORK, (1960).
PE-001	J.H.PERRY. CHEMICAL ENGINEERING HANDBOOK,MCGRAW HILL BOOK CO.,INC., 4TH EDITION(1963).
PE-002	V. PECHKOVSKII, A. KETOV, 'A STUDY OF THE THERMAL DECOMPOSITION OF ZINC SULFITE,' J. APPL. CHEM., VOL. 33, PP.1724-9 (1960).
PE-003	V.V. PECHKOVSKII, M.S. GAISINOVICH, RUSS. J. INORG. CHEM., VOL. 9, NO. 10, PP. 1245-7 (OCT. 1964).
PE-004	V.V. PECHKOVSKII, T.Y. MAL'TSEVA, ZHUR. PRIKL. KHIM., VOL. 37, NO. 2, PP. 240-5 (FEB. 1964).
PE-005	V.V. PECHKOVSKII, J. APPL. CHEM. USSR, VOL. 32, PP. 2691-6 (1959).

PR-001	N. H. PRATER, C. W. ANTONACCI, 'ESTIMATE FORCED-DRAFT FAN COSTS,' HYDROCARBON PROCESSING AND PETROLEUM REFINER, VOL. 40, NO. 7, PP. 129-39 (1961).
RE-001	A. REISMAN, J. AMER. CHEM. SOC., VOL. 80, PP.3558-9 (1958).
RE-002	L.A. REZNITSKII, ZH. FIZ. KHIM., VOL. 38, P. 760 (1964).(CHEMICAL ABSTRACTS,61:8004F.)
RE-003	RENEGADE AND CONSTEANU, BULL. SOC. CHIM. FRANCE, VOL. 15, P. 717 (1914).
RE-004	R. REMIREZ, 'GYPSUM FINDS NEW ROLE IN EASING SULFUR SHORTAGE,' CHEM. ENG., NO. 4, P. 112, (1969).
RE-005	RENEGADE AND CONSTEANU, COMPT. REND., VOL. 158, P. 946 (1914).
RO-001	W. ROTH, Z. ELEKTROCHEM., VOL. 46, P. 42 (1940).
RO-002	W.ROTH, ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA,XI, SECT. 12, 'THERMOCHEMISTRY (1931-1934),' HERMANN AND CO., PARIS, (1937).
RO-003	W. ROTH, G. BECKER, Z. PHYSIK. CHEM., VOL. A159, P. 1 (1932).
RO-004	T. ROSENQVIST, J. IRON AND STEEL INSTITUTE, VOL. 176, P. 36, (1954).
RO-005	W.A. ROTH, F I A T REPORTS OF GERMAN SCIENCE, INORG. CHEM., VOL. 4, P. 214 (1948).
RO-006	ROSSINI AND BICHOWSKY, THERMOCHEMISTRY OF CHEMICAL SUBSTANCES, NEW YORK (1936).
SA-001	P. SABATIER, ANN. CHIM. PHYS., VOL. 22, P.5 (1881).
SC-001	H. SCHAEFER, H. HEITLAND, Z. ANORG. CHEM., VOL. 304, P. 249, (1960).

SC-002	N. G. SCHMALL, E. MINZL, Z. PHYSIK. CHEM. (FRANKFURT), VOL. 47, P. 142 (1965).
SC-003	R. SCHENCK, P.VON DER FORST, Z. ANORG. CHEM., VOL. 241, PP. 145-57, (1939).
SC-004	SCHENCK AND RAUB, Z. ANORG. CHEM., VOL. 178, P. 225 (1929).
SC-005	R. SCHENCK, H. ROTERS, 'UBER DIE AKTIVIERUNG VON OXYDEN DURCH FREMDOXYDE,' Z. ANORG. CHEM., VOL. 211, PP. 65-82 (1933).
SC-006	R. SCHENCK, Z. ANGEW. CHEM., VOL. 49, P.649 (1936).
SC-007	N.G. SCHMAHL, F I A T REVIEW INORG. CHEM., VOL. 27, P.13.
SC-008	R. SCHENCK, 'KATALYTISCHE WIRKSAMKEIT UND GLEICHGEWICHT,' Z. ANORG. CHEM., VOL. 260, PP.154-60(1949).
SC-009	HERMANN SCHLICHTING, BOUNDARY LAYER THEORY, 4TH EDITION, MCGRAW-HILL BOCK CO., NEW YORK, (1960).
SH-001	C. SHOMATE, J. AM. CHEM. SOC., VOL. 68, PP. 964-6 (1946).
SH-002	SHOMATE, NAYLOR, AND BOERICKE, U. S. BUR. MINES, REPT. INVEST. NO. 3864 (1946), J. AM. CHEM. SOC., VOL. 68, P. 1003 (1946).
SI-001	SIMON AND THALER, Z. ANORG. CHEM., VOL. 162, P. 253 (1927).
SI-002	SIMON AND FEHER, Z. ELEKTROCHEM., VOL. 38, P. 143 (1932).
ST-001	J.R. STUBBLES, F.D. RICHARDSON, TRANS. FARADAY SOC., VOL. 56, P. 1460 (1960).
ST-002	R.P. STEIGER, E.D. CATER, J. PHYS. CHEM., VOL. 72, PP. 2231-3(1968).
ST-003	R. F. STEARNS, FLOW MEASUREMENT WITH ORIFICE METERS, D. VAN NOSTRAND COMPANY, INC. NEW YORK (1951).

SU-001	K. SUDO, SCIENCE REPT. RESEARCH INST. TOHOKU UNIV., SER.A, VOL. 2, P. 507 (1950).
SU-002	A. SUCHOV, B. BOROK, Z. MOROZOVA, 'THERMAL DECOMPOSITION OF CERTAIN SULFATES IN A CURRENT OF STEAM,' J. APPL. CHEM. USSR, VOL. 32, P. 1646, (1959).
TA-001	M. TAGAMI, W. BELL, J. PHYS. CHEM., VOL. 70, P. 3735 (1960).
TH-001	THOMSEN, THERMOCHEMISCHE UNTERSUCHUNGEN, BARTH, LEIPZIG (1882-1886).
TR-001	TRACOR VALUE ESTIMATED USING MODIFIED KOPP'S RULE, SEE TECHNICAL MEMORANDUM 004-009-CH4
TR-002	TRACOR VALUE ESTIMATED USING MODIFIED ERDOS METHOD, SEE TECHNICAL MEMORANDA 004-009-CH1 AND 004-009-CH1A.
TR-003	TRACOR VALUE ESTIMATED USING MODIFIED LATIMER METHOD, SEE TECHNICAL MEMORANDUM 004-009-CH5.
TR-004	HEAT CAPACITY OBTAINED BY SUMMING HEAT CAPACITIES OF CONSTITUENT OXIDES FROM TRACOR DATA BASE. SEE TECHNICAL MEMORANDUM 004-009-CH9.
TR-005	HEAT OF FORMATION OBTAINED BY COMBINING HEAT OF REACTION FROM LITERATURE WITH HEATS OF FORMATION FROM TRACOR DATA BASE.
TR-006	ABSOLUTE ENTROPY OBTAINED BY COMBINING ENTROPY OF REACTION FROM LITERATURE WITH ABSOLUTE ENTROPIES FROM TRACOR DATA BASE.
TR-007	ENTROPIES FOR TUNGSTATES AND MOLYBDATES ESTIMATED FROM OBSERVATIONS BASED ON RESULTS IN TECHNICAL MEMORANDUM 004-009-CH5.
TR-008	THE HEAT CAPACITY OF CRO3 WAS ESTIMATED FROM THE HEAT CAPACITIES OF WO3 AND MOO3.

TR-003	TRACOR VALUE ESTIMATED FROM OXIDE HEAT CAPACITY. SEE TECHNICAL MEMORANDUM C04-DC9-CH13.
TR-010	THIS VALUE HAS BEEN SELECTED AS THE BEST OF SEVERAL DIFFERENT REPORTED VALUES. SEE TECHNICAL MEMORANDUM 004-009-CH18
TR-011	M. TRAUTZ, S. PAKSCHWER, 'ZUR KENNTNIS DER SULFID-SULFAT REAKTION,' J. PRAKT. CHEM., PP. 147-81 (1929).
VA-001	V. A. VANYUKOV, N. A. KISELEVA, YUBELEINYI SBORNIK TRUDOV KAFEDRY I LAB. TYAZHELYKH METALLOV MOSKOV. INST. TSVETNYKH METALLOV I ZOLOTA NO. 7, P. 304, (1939).
WA-001	VON WARTENBERG, Z. ANORG. CHEM., VOL. 71, P. 427 (1911).
WA-002	J. S. WARNER, J. ELECTROCHEM. SOC., VOL. 114, P. 68 (1967).
WE-001	WESTRUM, ET AL., J. CHEM. PHYS., VOL. 35, P. 1670 (1961).
WE-003	A. WESTLAND, CAN. J. CHEM., VOL. 37., P. 1451 (1959).
WI-001	D. E. WILCOX, METHOD FOR ESTIMATING HEAT OF FORMATION OF INORGANIC COMPOUNDS, M. S. THESIS, UNIVERSITY OF CALIF., BERKLEY, CALIF., 1962.
WI-002	WISE, ET. AL., J. PHYS. CHEM., VOL. 66, P. 381 (1962).
WI-003	D. WILCOX, L. BROMLEY, IND. ENG. CHEM., JULY, 1963, PP. 32-9.
WO-001	WOHLER AND WITZMAN, Z. ELEKTROCHEM., VOL. 14, P. 97 (1908).
WO-002	WOHLER AND JOCKUM, Z. PHYSIK. CHEM., VOL. A167, P. 169 (1933).
WO-003	WOHLER, ZH. FIZ. KHIM., VOL. 167, P. 176 (1933).
WO-004	WOHLER AND MAHLA, ANN. CHEM. PHARM., VOL. 81, P. 255 (1852).

ZE-001 F. A. ZENZ, D. F. OTHMER, FLUIDIZATION AND FLUID PARTICLE SYSTEMS, REINHOLD PUBLISHING CORP., NEW YORK (1960).